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COMMUNICATIONS

Vibrational predissociation in OH-Ar^{a)}

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Although the spectroscopy and vibrational predissociation dynamics of closed shell van der Waals (vdW) systems have been extensively studied,¹⁻⁴ little is known about vdW interactions in open shell systems.^{5,6} Complexes of the hydroxyl radical with argon provide a model case for examining the intermolecular potential in an open shell system since OH-Ar is both experimentally observable⁷⁻⁹ and theoretically tractable.¹⁰ Spectroscopic studies^{7,8} have already illustrated the dramatic change in the OH-Ar potential upon electronic excitation of the OH moiety from the $X^2\Pi_{3/2}$ to the $A^2\Sigma^+$ state. The OH (center-of-mass) to Ar distance is substantially reduced ($\Delta r_e = 0.6 \text{ \AA}$) and Ar becomes much more tightly bound to OH, presumably due to charge transfer interactions¹⁰ in the excited electronic state correlating with OH $A(v' = 0) + \text{Ar}(^1S_0)$.

In this communication, we present results showing that the vibrational predissociation dynamics of OH-Ar differs greatly in its ground and excited electronic states.¹¹ The complexes are prepared with one quantum of OH vibrational excitation (v_{OH}), which is more than sufficient energy to break the OH-Ar bond. We report measurements of the vibrational predissociation lifetime and the nascent internal state distribution of the OH product.

In earlier work,^{7,8} we recorded the fluorescence excitation spectrum of OH-Ar in the region about the OH $A^2\Sigma^+(v' = 0) \leftarrow X^2\Pi_{3/2}(v'' = 0)$ transition (hereafter the OH 0-0 transition). A progression of bands was identified arising from excitation to vibrational levels of the OH-Ar stretching mode in the excited electronic state. In the present study, we scanned the probe laser in the vicinity of the OH 1-0 transition to find transitions which prepare the OH-Ar complexes with one quantum of OH vibrational excitation in the excited electronic state ($v'_{\text{OH}} = 1$). An OH-Ar progression was observed with elements positioned at 34 905.0, 35 042.7, 35 162.5, 35 264.0, and 35 347.0 cm^{-1} , as measured from the peak of the Q_1 branch. In addition, we searched the spectral region about the OH 1-1 transition to locate features originating from complexes containing one

quantum of OH vibrational excitation in the ground electronic state ($v''_{\text{OH}} = 1$). OH 1-1 lines¹² and a series of OH-Ar features were detected, the latter appearing at 31 474.9, 31 594.7, 31 696.2, and 31 779.2 cm^{-1} . Complexes of Ar with OH $X(v'' = 1)$ readily form and are evidently long-lived, persisting at least 30 μs after production. The OH-Ar progressions observed in the OH 1-0 and 1-1 regions show relative spacings and rotational structure similar to that of the progression associated with the OH 0-0 band.

Excitation of OH-Ar about the OH 0-0 transition results in resonant emission from the complex. By contrast, preparation of OH-Ar with one quantum of OH vibrational excitation in the excited electronic state results in a strong emission signal on the OH 0-0 transition centered at 309 nm, indicating rapid vibrational predissociation in the excited electronic state. No OH-Ar ($v'_{\text{OH}} = 1$) emission, which would appear in the region of the OH 1-1 emission at 315 nm, is observed. An upper limit for the vibrational predissociation lifetime of OH-Ar ($v'_{\text{OH}} = 1$), τ_{vp} , can be determined from the ratio of the emission signals in the 0-0 and 1-1 regions. At a monochromator resolution of 200 cm^{-1} , the height of the 0-0 emission peak relative to the wing at 315 nm gives $\tau_{\text{vp}} \leq \tau_r/70$, where τ_r is the radiative lifetime of OH-Ar. If τ_r is assumed equal to the radiative lifetime of OH $A(v' = 1)$, $\sim 700 \text{ ns}$,¹³ then an upper limit for τ_{vp} is 10 ns. A lower limit for τ_{vp} of 10 ps¹⁴ is derived from the laser bandwidth, since no lifetime broadening is observed in the excitation spectra.

For the three highest energy features in the OH-Ar progression about OH 1-0, higher resolution (60 cm^{-1}) dispersed fluorescence spectra have been recorded. No differences are observed among the three spectra. The emission profile from the OH $A(v' = 0)$ products is shown in Fig. 1. From the termination of the P_2 branch, it is evident that the OH product rotational distribution cuts off after $N = 7$ (944 cm^{-1}), corresponding to a classical impact parameter $b \leq 0.2 \text{ \AA}$. Although the rotational distribution cannot be uniquely determined from the emission spectrum at the present reso-

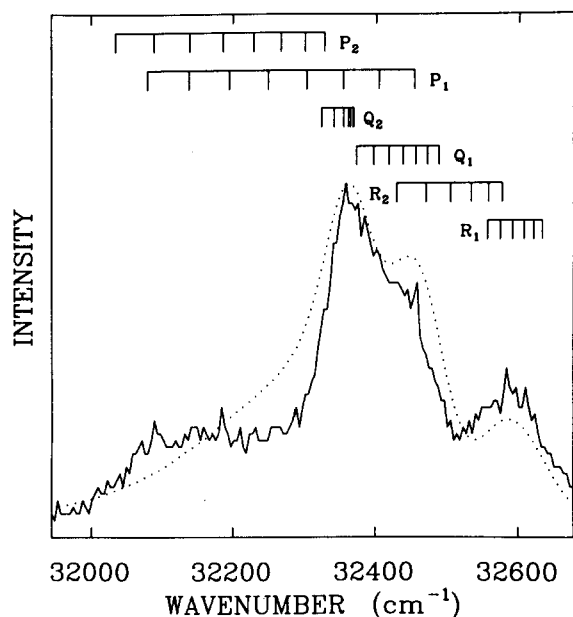


FIG. 1. Dispersed fluorescence spectrum from OH $A(v'=0)$ products on the 0-0 transition, following vibrational predissociation of OH-Ar complexes containing one quantum of OH vibrational excitation. The excitation laser was fixed on the OH-Ar feature at $35\,264.0\text{ cm}^{-1}$. The labels indicate OH transitions which contribute to the emission spectrum. Also shown (dotted line) is the simulated emission spectrum for a 600 K Boltzmann distribution of the OH product rotational levels.

lution, the population of OH product rotational levels clearly deviates from a Boltzmann distribution, as illustrated in Fig. 1. The nascent OH product rotational distribution falls off more slowly than a 600 K Boltzmann and then abruptly ends after $N=7$.

The cutoff in the OH product rotational distribution does not arise from a constraint on available energy. For the three levels examined, vibrational predissociation of OH-Ar releases more than 2500 cm^{-1} of excess energy to products, permitting OH product rotational levels as high as $N=11$ or 12 to be populated. The lower cutoff observed is consistent with restricted angular (bending) motion of the complex. Assuming that the forces during vibrational predissociation act along the line of centers between atoms gives $b \leq 0.06\text{ Å}$ ($N \leq 2$) if argon leaves from the oxygen side of the diatomic molecule. The production of OH $N=7$ products therefore requires that argon interact with the hydrogen end of the diatomic.

The rate of vibrational predissociation in OH-Ar com-

plexes is at least three orders of magnitude faster in the excited electronic state than in the ground electronic state. From the large energy mismatch between the OH and OH-Ar vdW vibrations, inefficient intramolecular energy transfer would be predicted in both electronic states.¹⁵ The marked increase in the rate of vibrational predissociation of OH-Ar upon electronic excitation points to an excited state interaction which effectively couples the OH vibration to the OH-Ar stretching mode. Analogous results have been obtained for vibrational relaxation of the OH radical, where vibrational energy transfer cross sections in the excited A state were found to be 10–1000 times greater than in the ground state with a variety of molecular collision partners.⁶ These experiments show that changes in the OH-Ar intermolecular potential upon electronic excitation of the OH radical are manifested in the full- and half-collision dynamics occurring on these surfaces.

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