

Symmetry-Dependent Branching between $O^+ + H$ and $O + H^+$ Dissociation Channels in the Photofragmentation of OH^+

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Laser excitation of OH^+ to rovibrational levels of the $c^1\Pi$ state results in predissociation to form $O^+ + H$ and $O + H^+$. Rotational levels with parity $-(-1)^J$ (f component) decay to form $O^+ + H$, whereas those of parity $+(-1)^J$ (e component) decay predominantly to form $O + H^+$. The branching is interpreted in terms of coupling of the $c^1\Pi$ state to nearby electronic states and dissociation continua. Signals are recorded by tunable dye-laser irradiation of a fast mass-selected beam of OH^+ and detection of O^+ ions or neutral oxygen atoms.

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Photodissociation of the OH^+ molecule is of particular interest because of the near degeneracy of the lowest $O^+(^4S) + H(^2S)$ and $O(^3P) + H^+$ dissociation asymptotes. Predissociated levels lying above these limits may, in principle, decay into either channel provided there is coupling between the bound levels and appropriate dissociation continua. We report here the observation of symmetry-dependent branching between these two fragmentation channels.

In a recent publication,¹ the detection of rotational lines of the 3-0 band in the $c^1\Pi$ - $b^1\Sigma$ system of OH^+ was described. The data were recorded by fast-ion-beam laser photofragment spectroscopy in which O^+ ions arising from predissociative decay of the laser-excited $c^1\Pi$ state were detected. It was noted¹ that the P ($\Delta J = -1$) and R ($\Delta J = +1$) lines were markedly weaker than those of the Q ($\Delta J = 0$) branch and could only be found for low values of J , the total angular momentum excluding nuclear spin. We report here the first laser-induced signals in the $O + H^+$ dissociation channel, obtained by direct detection of fast product neutral oxygen atoms. In sharp contrast to the earlier results, the P and R lines are found to be strong in the $O + H^+$ channel and the Q lines are absent. As the transitions with $\Delta J = \pm 1$ and 0 involve excited-state levels of different symmetry, this result shows a remarkable selectivity in the dissociative decay of OH^+ .

A laser photofragment study² of OH^+ using the ultraviolet lines of an argon-ion laser has demonstrated the importance of long-range nonadiabatic interactions close to the dissociation threshold. Shape resonances of the $A^3\Pi$ state were shown to decay to form O^+ ions, although this state correlates to the $O(^3P) + H^+$ asymptote. The branching ratio between dissociation channels was not determined but the method for detection of neutral oxygen atoms described in this Letter should not allow this to be achieved. In the work reported here, the predissociated $c^1\Pi$ levels lie about 1 eV above the dissociation limits and long-range nonadiabatic couplings between electronic states are expected to be of less importance.

Theoretical work to date on OH^+ includes calculation of electronic state energies and potential-energy curves,³⁻⁸ radiative and predissociation lifetimes of the $b^1\Sigma^+$ state,⁸ charge exchange and fine-structure excitation in $O-H^+$ collisions,⁹ and a study of long-range ion-atom potentials.¹⁰ A set of *ab initio* potential-energy curves⁶ is shown in Fig. 1; those of particular importance to this work are the optically connected $c^1\Pi$ and $b^1\Sigma^+$ states, the repulsive $^5\Sigma^-$ and $^3\Sigma^-$ states, and the $A^3\Pi$ state.

Laser photofragment spectroscopy is an established technique for spectroscopic and dynamical studies of ions¹¹ and the main features of our apparatus have been previously described.¹² Electron-impact ionization of H_2O in an ion source generates electronically and vibrationally excited OH^+ ions which are accelerated and formed into a mass-selected beam. Coaxial irradiation of the ion beam is achieved with a Coherent 699-29 tunable dye laser which promotes transitions from the meta-

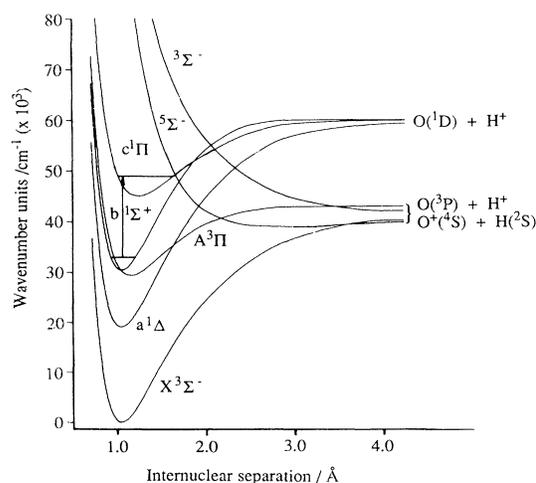


FIG. 1. Potential curves from Ref. 6 for the lowest state of OH^+ (reproduced with permission in modified form from Ref. 1).

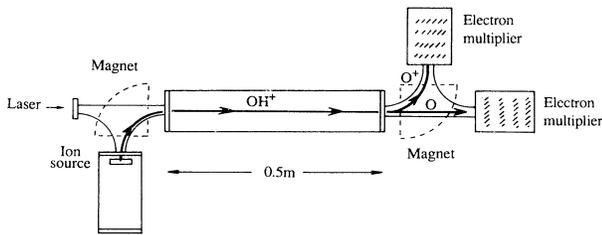


FIG. 2. Fast-ion-beam apparatus with on-axis detection of O atoms and mass-selected detection of O⁺ ions.

stable^{1,8} $b^1\Sigma^+$ state to levels of the $c^1\Pi$ state. In our earlier experiment,¹ predissociation of the excited levels was shown to result in the formation of the O⁺ ions which were separated from the OH⁺ beam with a second electromagnet and detected with an electron multiplier. This approach cannot be applied to the detection of H⁺ ions because the large center-of-mass kinetic energy release causes the protons to spread over a wide solid angle.² However, signals in the O+H⁺ channel can be recorded by detecting fast oxygen neutral atoms with an on-axis multiplier as shown in Fig. 2. Separation of H atoms from the O⁺+H channel and O atoms from the O+H⁺ channel is achieved by spatial discrimination due to the very different angular distributions of the two uncharged fragments. In both ion and neutral detection modes, the laser is chopped mechanically and a lock-in amplifier is employed. The impact of 0.5 W of cw dye-laser radiation on the first dynode of the on-axis electron multiplier has no detectable effect on its performance. The limiting spectroscopic linewidth of approximately 90

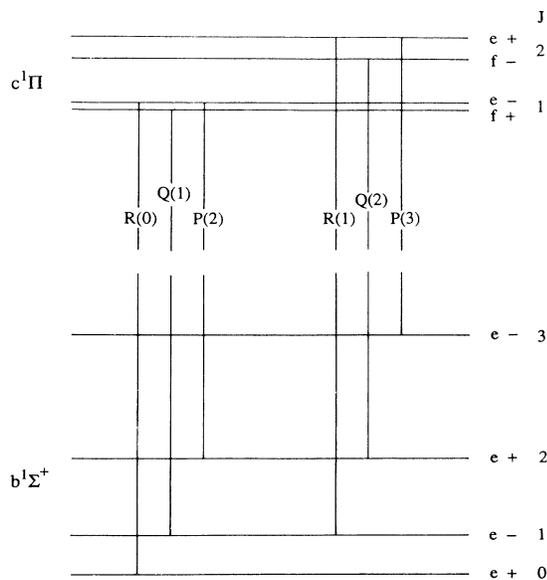


FIG. 3. Levels and rotational lines for a $^1\Pi$ - $^1\Sigma^+$ electronic transition. The lambda-doublet splittings are exaggerated by a factor of 20.

MHz is determined by the Doppler width of the ion beam and is sufficiently narrow to permit predissociation lifetime broadening to be observed.

The first rotational lines in a $^1\Pi$ - $^1\Sigma^+$ transition are illustrated in Fig. 3. Levels with parity $+(-1)^J$ are called e levels and those with parity $-(-1)^J$ are f levels.¹³ The lifting of the degeneracy in the $^1\Pi$ state for a given value of J is caused by the rotational-electronic interaction, principally with the $b^1\Sigma^+$ state, and the energy-level splitting is given approximately by $qJ(J+1)$, where q is the lambda-doubling parameter with value $0.0617(2) \text{ cm}^{-1}$ for $v=2$. The intensities of the rotational lines of the 2-0 vibrational band recorded in the O⁺ and O channels are given in Fig. 4. The Q lines involve excitation to levels of f -type symmetry and appear strongly in the O⁺+H channel whereas the P and R lines, which correspond to dissociation from e levels, are

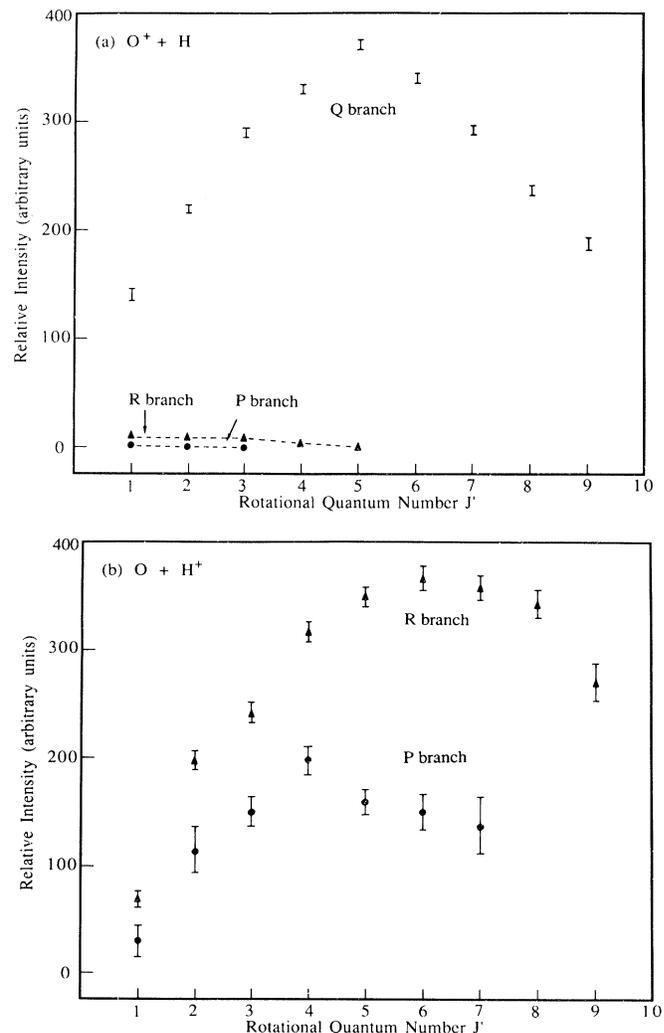


FIG. 4. Integrated experimental intensities in (a) O⁺+H and (b) O+H⁺ channels for excitation in P, Q, and R lines.

very weak and decrease in intensity with increase in J' value. In contrast, the P and R lines are strong in the $O+H^+$ channel and the Q lines are absent. There is therefore a symmetry-selective partitioning between channels for f levels, and a propensity for e levels to decay to form $O+H^+$. The higher members of the P and R branches of the 2-0 band exhibit predissociation lifetime broadening and Fig. 5 shows that the experimental linewidth for the e levels with $J' > 3$ depends linearly on $J'(J'+1)$. In summary, we conclude that the O^++H channel is open for decay of both e and f levels but an additional J -dependent predissociation mechanism leading to formation of $O+H^+$ also operates for e levels.

In principle, a large number of predissociation mechanisms can lead to dissociative decay of the $c^1\Pi$ state. From the potential-energy curves of Fig. 1, it is seen that the $c^1\Pi$ state is crossed by repulsive curves of $^5\Sigma^-$ and $^3\Sigma^-$ symmetry. The repulsive $^3\Sigma^-$ state appears to lie too far above $v=2$ of the $c^1\Pi$ state to make a major contribution to the predissociation rate. Both e and f components of the $c^1\Pi$ state are predissociated by the $^5\Sigma^-$ state which, in the absence of mixing at long range with states correlating to the nearby $O+H^+$ channel, correlates to O^++H . The mechanisms for the $^1\Pi$ - $^5\Sigma^-$ interaction are spin-spin and second-order spin-orbit coupling¹⁴ and calculations in a Hund's case (b) basis show that there is no major difference in the coupling matrix elements for e and f levels. We conclude that although coupling to the $^5\Sigma^-$ state is the likely decay route for f levels and also occurs for levels of e -type symmetry, it cannot explain the observed symmetry-selective decay.

The major difference between the e and f components of the $c^1\Pi$ state is the mixing of the e levels with the nearby $b^1\Sigma^+$ state under the action of the rotational-electronic operator. The lambda-doublet splitting in the $c^1\Pi$ state is one manifestation of this interaction. How-

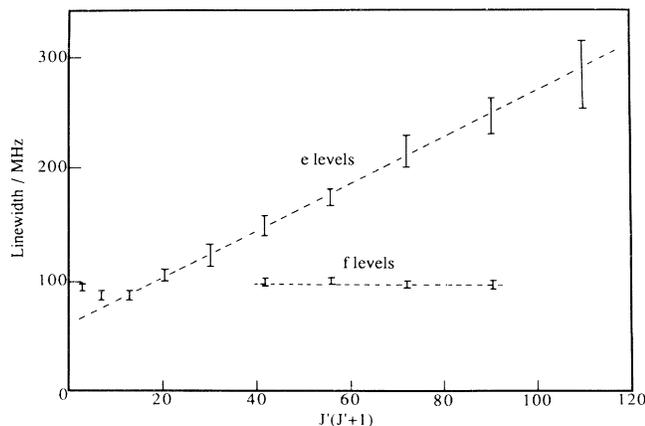


FIG. 5. Experimental linewidth Γ vs $J'(J'+1)$ for e levels detected in the $O+H^+$ channel and f levels with $5 < J' < 10$ in the O^++H channel.

ever, this mixing does not provide a direct dissociative decay route because the $b^1\Sigma^+$ state correlates to the energetically inaccessible $O(^1D)+H^+$ limit. However, Fig. 1 shows that there is good overlap between the repulsive parts of the $b^1\Sigma^+$ and $A^3\Pi$ curves at the inner turning points near 0.8-Å internuclear separation. Spin-orbit interaction between these states causes the levels of the $b^1\Sigma^+$ state to be quite strongly predissociated; the calculated predissociation lifetimes for $v=5-7$ of the $b^1\Sigma^+$ state are 2-3 ps.⁸ Therefore the $b^1\Sigma^+$ state can act as a "doorway" state for dissociation of $c^1\Pi$ levels into the continuum of the $A^3\Pi$ state which correlates to the $O(^3P)+H^+$ dissociation limit. A demanding test of this hypothesis is the calculation of predissociation lifetimes for the e levels which may then be compared with the data presented in Fig. 5.

The linewidth $\Gamma_{v(\Pi)}$ for a vibrational level $v(\Pi)$ of the $c^1\Pi$ state can be expressed

$$\Gamma_{v(\Pi)} = \Gamma_{v(\Sigma)} [\langle ^1\Pi | L_+ | ^1\Sigma^+ \rangle]^2 \times J(J+1) \left[\sum_{v(\Sigma)} \frac{B_{v(\Pi),v(\Sigma)}}{|\Delta E_{v(\Pi),v(\Sigma)}|} \right]^2,$$

where $\Gamma_{v(\Sigma)}$ is the predissociation linewidth for vibrational level v of the $b^1\Sigma^+$ state arising from spin-orbit interaction with the $A^3\Pi$ continuum,⁸ $\langle ^1\Pi | L_+ | ^1\Sigma^+ \rangle$ is the matrix element of the rotational-electronic operator,

$$B_{v(\Pi),v(\Sigma)} = \langle v(\Pi) | h^2/8\pi^2\mu R^2 | v(\Sigma) \rangle,$$

and $\Delta E_{v(\Pi),v(\Sigma)}$ is the vibrational energy-level separation. The values of $B_{v(\Pi),v(\Sigma)}$ were calculated by numerical integration using the vibrational wave functions derived from experimental Rydberg-Klein-Rees $c^1\Pi$ and *ab initio*⁶ $b^1\Sigma^+$ potential-energy curves. Use of experimental curves for the $b^1\Sigma^+$ and $A^3\Pi$ states would be preferred but these data are not yet available. The value of the matrix element $\langle ^1\Pi | L_+ | ^1\Sigma^+ \rangle$ was determined from the experimental lambda-doubling parameter q , and the linewidths of the $b^1\Sigma^+$ levels were taken from Ref. 8. The calculated widths range between 7.3 MHz for $J'(e)=1$ and 330 MHz for $J'(e)=9$, compared with an experimental width of 260(20) MHz for $J'(e)=9$. The agreement between the theoretical and experimental linewidths is therefore very good and the observed $J(J+1)$ dependence is also reproduced. It is of interest to note that a similar symmetry-selective effect occurs in electron autodetachment from the NH^- molecule.^{15,16}

In summary, we have found that a symmetry-selective rotational-electronic mechanism operates in the predissociation of OH^+ ($c^1\Pi$) and induces partitioning between the O^++H and $O+H^+$ dissociation channels. Experimental and theoretical studies of dissociation from other vibrational levels, spectroscopic assignments of lines in both $c^1\Pi$ - $b^1\Sigma^+$ and $c^1\Pi$ - $a^1\Delta$ band systems, and full details of the calculations described here will be reported in future papers.

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