A study of the structure and dynamics of the hydronium ion by high resolution infrared laser spectroscopy. III. The $\nu_3$ band of $\text{D}_3\text{O}^+$

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294 transitions were measured by velocity modulation spectroscopy using a difference frequency laser system with a $\text{D}_2\text{O}$ discharge and assigned to the $\nu_3$ (antisymmetric stretch) band of $\text{D}_3\text{O}^+$. A simultaneous analysis of this data with the $\nu_2$ band spectra reported by Sears et al. [J. Chem. Phys. 83, 2676 (1985)] yielded a refined set of parameters for both the ground and the excited states of both bands. The $\nu_3$ bandcenters are 2629.6512(39) and 2624.2376(47) cm$^{-1}$ for the $s-s$ and $a-a$ inversion components, respectively.

INTRODUCTION

Despite the fact that the hydronium ion (H$_3$O$^+$) is perhaps the most fundamentally important molecular ion in chemistry, its structure and properties had not been studied in detail until 1983. The revolutionary progress realized in infrared spectroscopy of molecular ions within the last decade has now made this species amenable to detailed investigation with several highly precise methods. Similarly, much theoretical work has been done to characterize the molecular properties of H$_3$O$^+$ with high level $ab$ initio calculations, the results of which have proven most useful for guiding laboratory investigations.

Following our initial detection of the $\nu_3$ vibrational band with velocity modulation laser spectroscopy, which was guided by the calculations of Colvin et al., a great deal of experimental work emerged. Detailed investigations were conducted on the $\nu_6$ and $\nu_4$ fundamental bands and the $\nu_3$ fundamental and hot bands of H$_3$O$^+$. Through combination differences between several $\nu_3$ bands, Liu and Oka first determined the ground state inversion splitting as 55.35 cm$^{-1}$.

With such a large inversion splitting, e.g., compared to the 0.79 cm$^{-1}$ value for NH$_3$, pure inversion and inversion–rotation transitions for H$_3$O$^+$ occur in the far-IR region, where they have recently been measured to high precision. Detection of the $\nu_3 + \nu_3 - \nu_2$ s-s hot band of H$_3$O$^+$ and the $\nu_2$ (1$-0^+$) fundamental band of H$_3$O$^+$ has recently been reported. In the first measurement for the D$_3$O$^+$ isotope, Sears et al. measured the $\nu_2$ fundamental band. Also reported in Ref. 25 was a semipirical determination of the structure and molecular potential for H$_3$O$^+$ using the nonrigid bender Hamiltonian, which accounts for the large amplitude inversion motion by parametrizing it separately from the other degrees of freedom; by combining experimental and $ab$ initio data, the resulting molecular potential was reasonably successful in describing some of the spectroscopic properties of H$_3$O$^+$, but produced unsatisfactory agreement with the $\nu_4$ fundamental band, which was measured subsequently at Berkeley. Recently obtained experimental data was again supplemented with $ab$ initio data in a similar fit using the nonrigid inverter Hamiltonian method to produce a refined potential and improved spectroscopic constants.

In this paper, we describe measurements made for the D$_3$O$^+$ isotope using velocity modulation laser spectroscopy with a difference frequency laser. Both the $s-s$ and $a-a$ inversion components have been measured and analyzed in a simultaneous, weighted least-squares analysis of the $\nu_2$ band transitions reported by Sears et al. As a result of several modifications in the $\nu_2$ $a-s$ band assignments given in Ref. 25, improved spectroscopic constants are obtained for the ground state of $\nu_3$ and excited state of $\nu_3$. These, along with the constants for the excited $\nu_3$ levels from the measurements described below, should contribute to an improved determination of the molecular potential for H$_3$O$^+$.

EXPERIMENTAL

The spectrometer used in this work has been described in detail in connection with our earlier work on DN$_2$$^+$. In a 70 cm discharge cell with a 0.5 cm bore, D$_3$O$^+$ is generated in a water cooled discharge through a 10:1 mixture of D$_2$ and O$_2$ at a total pressure of 1.0–1.5 Torr. The discharge is driven at a frequency of 1.7 kHz and a current density of 60 mA/cm$^2$.

The difference frequency laser source is analogous to the one developed by Pine and has also been described previously. By mixing the radiation from a single mode Ar$^+$ laser with that from a single-mode ring dye laser (Rhodamine 6G) in a temperature phase matched LiNbO$_3$...
crystal, \( \sim 10 \, \mu \text{W} \) of narrow-band (\(< 0.001 \, \text{cm}^{-1}\)) infrared radiation is produced. Tuning (2.2–4.2 \( \mu \)) is achieved by scanning both the dye laser and the crystal temperature, which is controlled by a servo loop and microcomputer. Typical scan lengths in the infrared spectrometer would exceed 2.5 \( \text{cm}^{-1} \) (4096 channels at 20 MHz/channel), requiring approximately 15 min per scan. Absolute and relative frequency markers for the dye laser were obtained by monitoring \( I_2 \) fluorescence and transmission fringes from a confocal etalon, respectively. Both visible lasers are measured to \(< 10^6 \) accuracy with a commercial wavemeter, so that the absolute uncertainty in the infrared frequency, from the difference in the two visible frequencies, is near 0.02 \( \text{cm}^{-1} \), being limited by the drift in the unstabilized \( \text{Ar}^+ \) laser.

The infrared beam is split to permit background subtraction, which minimizes the contribution from laser noise amplitude fluctuations; one of the beams is sent axially down the discharge cell to the sample detector, with the other impinging on a reference detector (liquid nitrogen cooled InSb, 0.25 \( \times \) 0.25 cm). Signals are electronically subtracted before going to a lock-in amplifier for phase sensitive detection at the discharge frequency (1 kHz) with a 125 ms time constant. The output is sampled via a microprocessor controlled A/D converter which permits signal averaging. A stick spectrum of the observed transitions is given in Fig. 1. Sensitivity for absorption in the dual beam configuration is on the order of \( 10^{-6} \) at 1.7 kHz with a 125 ms time constant, i.e., within a factor of 5 of the shot noise detection limit.

**RESULTS AND ANALYSIS**

In the region 2540–2730 \( \text{cm}^{-1} \), approximately 400 transitions were observed that clearly originated from a positive ion, as indicated by their derivative-like \( 1f \) line-shapes. The initial assignment to the \( \nu_3 \) band of \( \text{D}_3\text{O}^+ \) was made by comparing the experimental line positions and intensities with calculated patterns generated using ground state constants from the \( \nu_3 \) band reported by Sears et al. and estimates for the \( \nu_3 \) band constants. Transition frequencies were fit with a least-squares analysis to differences between term values for the ground and excited vibrational states using the normal selection rules for a perpendicular band of a symmetric top with inversion (\( \Delta \kappa = \pm 1 \), \( \Delta J = 0, \pm 1 \)) for transitions occurring without a change in inversion quantum number, i.e., \( s \rightarrow s \) and \( a \rightarrow a \). The eigenvalues were calculated using the standard form for an oblate symmetric top including up to quartic distortion terms. The nondegenerate ground state energies are given by

\[
E_0(J,K) = B''J(J+1) + (C'' - B'')K^2 - D''J^2 \times (J+1)^2 - D''J(J+1)K^2 + D''_K K^4.
\]

(1)

Theoretical values predicted by \( \tilde{S} \)pirko and Bunker were used to estimate \( C'' \). For the doubly degenerate excited \( \nu_3 \) vibration–rotational levels, the expression takes the form

\[
E_3(J,K,l) = v_0 + B'J(J+1) + (C' - B')K^2 - 2(\xi C')Kl - D'J(J+1)^2 - D''J(J+1)K^2 + D''_K K^4 + \eta J(J+1)Kl + \eta_k K^4.
\]

(2)

Assignments were made with reference to intensities and combination differences, the latter being used both for internal self-consistency and for consistency with the results from Ref. 25. In the initial stages of the analysis, the ground-state constants were fixed at the values from the analysis of the \( \nu_3 \) spectrum reported by Sears et al. The symmetric inversion component of the \( \nu_3 \) band was easier to analyze since the assignment of the \( \nu_2 \) \( s \rightarrow a \) band is more complete than that of the \( a \rightarrow s \) band, such that constants...
and calculated combination differences for the $0^+$ state are more precise than for $0^-$. The final analysis was performed with a weighted least-squares fit including both the $\nu_1$ band and the $\nu_2$ band line positions. Transitions were weighted by the inverse square of their respective experimental uncertainty, which was taken to be 0.020 and 0.001 cm$^{-1}$ for the $\nu_1$ and $\nu_2$ data, respectively, yielding a fit in which each component of the data set is fit close to the experimental uncertainty ($\chi^2$ = 1). For the $s$-$s$ band, the final fit also included sextic distortion terms for the $\nu_2$ terms only. The terms $\eta_2$ and $\eta_4$ were not determined at the 2σ confidence level, hence they were not included; consequently, $D'_{\nu_2}$ and $D''_{\nu_2}$ are effective parameters. For the symmetric band, 171 transitions from the $\nu_2$ band were included with quantum numbers up to $J,K = 13$. The derived parameters are given in Table I. A complete version of the results, including transition frequencies and residuals, is available in a supplemental publication.\textsuperscript{30}

For the $\nu_3$ a-a band, it was not possible to extend the assignment to high $K$ when constrained by the $0^-$ ground state constants reported in Ref. 25. By excluding one of the previously assigned lines in the $\nu_2$ a-s band [Q$_a$(9)] and allowing the ground-state constants to vary in a combined fit which included the remaining $\nu_2$ band lines, the transitions for the $\nu_3$ band, including those with high $K$, produced a satisfactory fit. The transition deleted from the original assignment by Sears \textit{et al.}, for the $\nu_2$ band was the only one with $K > 5$. With the parameters derived from this work, it was possible to assign four other previously unassigned lines in the $\nu_2$ band which were reported in Ref. 25, viz. Q$_{a}(7)$, R$_a(9)$, R$_a(10)$, and R$_a(12)$. It was then possible to include 123 transitions in the $\nu_3$ a-a band fit, performed as described above for the $s$-$s$ band, except without including any sextic distortion constants. The parameters from the fit are given in Table II, where a more complete version is again provided elsewhere.\textsuperscript{30}

**DISCUSSION**

The constants most affected by the new assignments in the $\nu_3$ band are $D_{JK}(0^-)$ and $D_{JK}(\nu_2 = 1^+)$. These are reduced by more than a factor of 2, and are more consistent with those from the semiempirical anharmonic potential given by Špirko and Kraemer.\textsuperscript{26} While the $\nu_3$ a-a band assignment is less complete than that for the $s$-$s$ component, its validity is established by the fact that it yielded constants which led to a refinement of the $\nu_2$ a-a band analysis.

The band centers for the $s$-$s$ and a-a components of the $\nu_3$ band of D$_2$O$^+$ (2629.65 and 2924.24 cm$^{-1}$, respectively) are approximately 35 cm$^{-1}$ higher than those predicted by Špirko and Kraemer.\textsuperscript{26} The difference between the band centers represents the difference in inversion splittings between the ground and excited $\nu_3$ states. The estimate of this difference from the anharmonic potential (7.41 cm$^{-1}$) is in good agreement with our experimental result (5.41 cm$^{-1}$). The value obtained from the potential determined from a fit of the inversion potential constants to the existing experimental information (Fit I in Ref. 26) is better than that in which the inversion parameters were fit to purely \textit{ab initio} points (Fit II). The experimentally determined variations in rotational and centrifugal distortion constants which occur with a single quantum of $\nu_3$ excitation are reasonable based upon extrapolations from H$_2$O$^+$ and ND$_3$.\textsuperscript{31} The results of this work will be useful not only for additional refining of the molecular potential for H$_2$O$^+$, but also for improving predictions of far-IR inversion and inversion–rotation transitions for D$_2$O$^+$ by providing a set of refined ground state molecular constants.

**TABLE I. Combined fit of the $\nu_3$ s-s and the $\nu_2$ s-a bands of D$_2$O$^+$.**

<table>
<thead>
<tr>
<th>Constant (cm$^{-1}$)</th>
<th>Ground state (s)$^b$</th>
<th>$\nu_1(a)$</th>
<th>$\nu_1(s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>0</td>
<td>645.130 43(37)</td>
<td>2629.631 14(47)</td>
</tr>
<tr>
<td>$B$</td>
<td>5.674 981(61)</td>
<td>5.564 325(57)</td>
<td>5.594 96(29)</td>
</tr>
<tr>
<td>$C$</td>
<td>3.08$^c$</td>
<td>3.093 751(13)</td>
<td>3.073 44(42)</td>
</tr>
<tr>
<td>$D'_J$</td>
<td>0.285 08(82)</td>
<td>0.187 37(65)</td>
<td>0.292 44(55)</td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>0.564 22(22)</td>
<td>0.292 17(11)</td>
<td>0.660 (12)</td>
</tr>
<tr>
<td>$D_K$</td>
<td>0.347 2(35)</td>
<td>0.154 53(33)</td>
<td>0.369 (11)</td>
</tr>
<tr>
<td>$H'_J$</td>
<td>0.039 (18)</td>
<td>0.039 (18)</td>
<td>0.039 (18)</td>
</tr>
<tr>
<td>$H_{JK}$</td>
<td>0.0254 (60)</td>
<td>0.0254 (60)</td>
<td>0.0254 (60)</td>
</tr>
<tr>
<td>$H_K$</td>
<td>1.93 (11)</td>
<td>1.93 (11)</td>
<td>1.93 (11)</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.162 37(12)</td>
<td>0.162 37(12)</td>
<td>0.162 37(12)</td>
</tr>
</tbody>
</table>

$\chi^2$ of all included data: 0.896 for 230 lines
$\chi^2$ of $\nu_1$ band data: 0.855 for 171 lines
$\chi^2$ of $\nu_2$ band data: 1.04 for 49 lines

\textsuperscript{a}Quoted 1 $\sigma$ uncertainties are given in parentheses and the correlation table is available from the authors upon request.
\textsuperscript{b}Inversion component.
\textsuperscript{c}Fixed at \textit{ab initio} value from Ref. 2.
\textsuperscript{d}Quartic centrifugal distortion constants are in units of 10$^{-3}$ cm$^{-1}$.

**TABLE II. Combined fit of the $\nu_3$ a-a and $\nu_2$ a-s bands of D$_2$O$^+$.**

<table>
<thead>
<tr>
<th>Constant (cm$^{-1}$)</th>
<th>Ground state (a)$^b$</th>
<th>$\nu_1(s)$</th>
<th>$\nu_1(a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>0</td>
<td>438.386 19(61)</td>
<td>2624.204 5(49)</td>
</tr>
<tr>
<td>$B$</td>
<td>5.643 650(80)</td>
<td>5.734 736(79)</td>
<td>5.579 11(26)</td>
</tr>
<tr>
<td>$C$</td>
<td>3.09$^c$</td>
<td>3.004 621(43)</td>
<td>3.078 64(21)</td>
</tr>
<tr>
<td>$D'_J$</td>
<td>0.252 41(34)</td>
<td>0.236 53(42)</td>
<td>0.426 49(29)</td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>0.363 11(55)</td>
<td>0.312 14(49)</td>
<td>0.574 76(44)</td>
</tr>
<tr>
<td>$D_K$</td>
<td>0.266 54(11)</td>
<td>0.204 82(42)</td>
<td>0.176 96(46)</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.159 27(15)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\chi^2$ of all included data: 1.26 for 154 lines
$\chi^2$ of $\nu_1$ band data: 1.28 for 123 lines
$\chi^2$ of $\nu_2$ band data: 1.20 for 31 lines

\textsuperscript{a}Quoted 1 $\sigma$ uncertainties are given in parentheses and the correlation table is available from the authors upon request.
\textsuperscript{b}Inversion component.
\textsuperscript{c}Fixed at \textit{ab initio} value from Ref. 2.
\textsuperscript{d}Quartic centrifugal distortion constants are in units of 10$^{-3}$ cm$^{-1}$. 
ACKNOWLEDGMENTS

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