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Observation of $\Delta|k-l|=3$ Transitions in the ν_3 Band of H_3O^+

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Although the vibration–rotation spectrum of H_3O^+ has been studied extensively, there has been no experimental information on the value of the C rotational constant because of the absence of any observed $\Delta|k-l| \neq 0$ forbidden transitions. However, as pointed out by Verhoeve *et al.* in their far-infrared spectroscopic work [P. Verhoeve, M. Versluis, J. J. Ter Meulen, W. L. Meerts, and A. Dynamus, *Chem. Phys. Lett.* **161,** 195–201 (1989)], a near degeneracy exists between some $(J, 0)^+$ and $(J, 3)^-$ ground state rotation–inversion levels, which causes sizable shifts in these levels due to off-diagonal centrifugal distortion. These shifts were observed in the ground state combination differences of the ν_3 fundamental transitions. We have observed 11 forbidden $\Delta|k-l|=3$ transitions to the ν_3 band induced by the mixing in the ground state and involving the $J=7$, 9, and 11 levels, and determined the energy difference between different K levels, the C rotational constant, and the off-diagonal centrifugal distortion mixing coefficient. © 1997 Academic Press

INTRODUCTION

Over the past decade, the vibration–inversion–rotation spectrum of the H_3O^+ ion has been investigated by experimentalists and theoreticians since its first high-resolution gas phase spectrum in the 3 μm region was reported in 1983 (*1*). It is a fundamental molecular ion crucial in many biochemical and organic reactions and in the ion-molecule reaction scheme in dense interstellar clouds (*2*). H_3O^+ is structurally and dynamically similar to its isoelectronic species NH_3 with its pyramidal structure and rotation–vibration levels split by inversion. In the ground vibrational state, it has a large inversion splitting of 55.34 cm^{-1} (*3, 4*). Since this value happens to be close to 9 $(B-C)$, there exists a near degeneracy between the $(J, K=0)$ levels in the $(+)$ inversion state and the $(J, K=3)$ levels in the $(-)$ inversion state for odd values of J. The two levels are closest at $J=9$ and considerable mixing of these levels is expected. The rotation of the molecule perpendicular to the symmetry axis induces a small dipole moment by centrifugal distortion (*5*), which mixes the $|J, K=0, 0^+\rangle$ and $|J, K=3, 0^-\rangle$ levels. Thus, it has been predicted (*4, 6, 7*) that forbidden $\Delta k=3$ transitions may be observable in the ν_2 band of H_3O^+. Similar transitions have been detected due to similar mixing in the ν_2 state of NH_3 (*8, 9*).

In this article, we report our observation of 11 forbidden $\Delta|k-l|=3$ transitions in the ν_3 band of H_3O^+ due to $\Delta k=\pm 3$ mixing in the ground state. They were detected following our observation of shifts in the $K=3$ antisymmetric ground state levels while working on an extended analysis of the ν_3 band. Although the vibration–rotation spectrum of H_3O^+ has been studied extensively, no $\Delta|k-l|\neq 0$ transitions have been previously assigned and experimental information on the C rotational constant has not been available. The $\Delta|k-l|=3$ transitions we obtained enabled us to determine the energy difference between the different K levels and thus the values of $C-9D_{kk}$ and the mixing coefficient.

EXPERIMENTAL

The spectrum of H_3O^+ was obtained using either a difference frequency laser spectrometer (*10*) or a color center laser spectrometer (*11*) with the velocity modulation technique (*12*). In the difference frequency spectrometer, the radiation from a single-mode Ar ion laser and a tunable ring dye laser are combined in a temperature-controlled $LiNbO_3$ crystal to generate infrared radiation with a frequency of $\nu_{Ar}-\nu_{dye}$. With the color center spectrometer, infrared radiation is generated by pumping an F_A(II)-type RbCl:Li crystal by a Kr ion laser, which was tuned by scanning the voltage of a piezoelectrically controlled intracavity étalon while the grating was slowly adjusted. In both systems, 10% of the infrared radiation generated was sent to a reference gas for frequency calibration while the remaining portion of the radiation was directed to a water-cooled ac glow discharge where H_3O^+ was produced. The infrared radiation was divided into two beams of equal power, with each beam traversing the discharge cell three or four times unidirectionally in a modified White cell configuration. It was then sent to two matched InSb detectors where the detected signals were combined in opposite phase in a pair of audio frequency transformers and sent

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to a lock-in amplifier for signal amplification. The signals were simultaneously recorded with a chart recorder and a computer.

The H_3O^+ ions were produced using three different gas mixtures: (a) 100 mT H_2, 100 mT O_2, 10 Torr He; (b) 250–450 mT of gas from a 50% H_2O_2–water solution and 7 Torr He; and (c) 550 mT H_2 and 150 mT O_2. The discharge was powered by either a Plasmalok RS-8 operating at 25 kHz or an audio amplifier (Tecron 7550) coupled to a step-up transformer at 6 kHz. The voltage and current were about 10 kV and 300 mA with the Plasmalok, and approximately half of these with the audio amplifier and transformer. The glass discharge cells were 1 meter long with inner diameters of 12 and 18 mm and multiple gas inlets and outlets running along their lengths. Wavenumber calibration was provided by spectral lines of NH_3 (*13*) and H_2O (*14*). The accuracy of the frequency measurement was 0.01 cm^{-1} for the color center spectrometer and 0.006 cm^{-1} for the difference frequency spectrometer.

EXPERIMENTAL GROUND STATE COMBINATION DIFFERENCES AND $\Delta k = 3$ MIXING

Because of the inversion motion of H_3O^+ with D_{3h} symmetry, its ground vibrational state splits into a symmetric $|0^+\rangle$ level with A_1' symmetry and an antisymmetric $|0^-\rangle$ level with A_2'' symmetry. From nuclear spin statistics and the Pauli principle, only J = odd levels are allowed for $K = 0$ in the $|0^+\rangle$ state and J = even levels for the $K = 0$ $|0^-\rangle$ state. Because of the rotational parity of $(-1)^K$ and the selection rule $\Delta K = \pm 1$, the ν_3–0 transition is allowed between symmetric–symmetric and antisymmetric–antisymmetric vibration–inversion states, with the usual selection rules of $\Delta J = 0, \pm 1$.

The ν_3 band of H_3O^+ has been previously studied by several workers (*1, 11, 15–17*). While we were extending the analysis of this band to higher J and K rotational levels, we observed large differences between the experimental and calculated ground state combination differences for the antisymmetric band for $K = 3$ levels (See Table 1). The ground state combination differences were calculated from the usual energy level expression for an oblate symmetric top

$$\begin{aligned} E(J,K) = {} & BJ(J+1) + (C-B)K^2 - D_{ij}J^2(J+1)^2 \\ & - D_{jk}J(J+1)K^2 - D_{kk}K^4 + H_{jjj}J^3(J+1)^3 \\ & + H_{jjk}J^2(J+1)^2K^2 + H_{jkk}J(J+1)K^4 \\ & + H_{kkk}K^6 \end{aligned} \quad [1]$$

using the constants given in Ref. (*4*) which are derived from the far infrared rotation–inversion spectrum. From the values of the discrepancy between the observed and calculated, it was clear that the odd J levels with $K = 3$ were perturbed by nearby levels while even J levels were unshifted. This reminded us of the work by Verhoeve *et al.* (*4*) who suggested that the shifts in the $|J =$ odd, $K = 3, 0^-\rangle$ levels were due to the presence of the $|J =$ odd, $K = 0, 0^+\rangle$ levels, while the $|J =$ even, $K = 3, 0^-\rangle$ states were unperturbed because $|J =$ even, $K = 0, 0^+\rangle$ were nonexistent. These pairs of levels have the same symmetry since the rotational parity of a symmetric top is $(-1)^K$.

TABLE 1

Observed and Calculated Ground State Combination Differences in the $|0^-\rangle$ State, from $^rQ(J,3) - {}^rP(J+1,3)$ (left column) and $^pQ(J,3) - {}^pP(J+1,3)$ (right column) in cm^{-1}

(J + 1, 3) - (J, 3)	Experimental	obs-calc	(J + 1, 3) - (J, 3)	Experimental	obs-calc
5,3 - 4,3	110.204	-0.006	5,3 - 4,3	110.218	0.008
6,3 - 5,3	131.976	-0.010	6,3 - 5,3	131.988	0.002
7,3 - 6,3	153.658	0.038	7,3 - 6,3	153.663	0.043
8,3 - 7,3	175.050	-0.038	8,3 - 7,3	175.049	-0.039
9,3 -8,3	196.202	-0.167	9,3 -8,3	196.192	-0.177
10,3 - 9,3	217.647	0.205	10,3 - 9,3	217.652	0.210
11,3 - 10,3	238.149	-0.137	11,3 - 10,3	238.145	-0.141
12,3 - 11,3	259.012	0.130			

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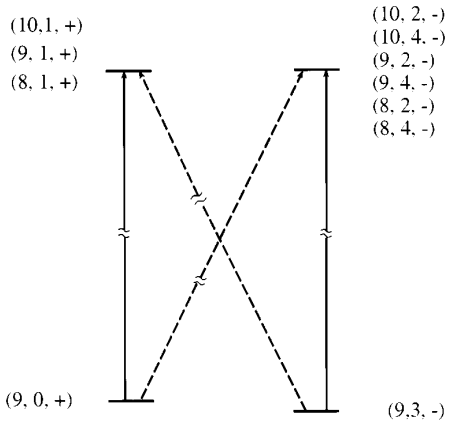

FIG. 1. The allowed and forbidden transitions to the ν_3 band of H_3O^+ due to the mixing of the (9, 0, 0^+) and the (9, 3, 0^+) levels. The solid lines denote the allowed transitions while the broken lines denote the forbidden $\Delta|k-l| = 3$ transitions due to the intensity borrowing.

In inverting C_{3v} molecules such as NH_3 and H_3O^+, there are centrifugal distortion terms that mix states differing by $\Delta k = 3$ (*18*),

$$H' = \alpha' Q_2[(J_+^3 + J_-^3)J_z + J_z(J_+^3 + J_-^3)] + i\beta' P_2(J_+^3 + J_-^3), \quad [2]$$

where α' and β' are the off-diagonal centrifugal distortion constants and $J_\pm = J_x \mp iJ_y$. Q_2 and P_2 are the coordinate and momentum, respectively, of the inversion motion. The matrix element connecting the pair of perturbed levels $|J, K = 3, 0^-\rangle$ and $|J, K = 0, 0^+\rangle$ states is then

$$\langle J, 0, 0^+|H'|J, 3, 0^-\rangle = \sqrt{2}(3\alpha - \beta) \times [(J+3)!/(J-3)!]^{1/2} \equiv \delta, \quad [3]$$

where $\alpha = \alpha'\langle 0^+|Q_2|0^-\rangle$ and $\beta = -\beta'\langle 0^+|iP_2|0^-\rangle$.

The sizable observed shifts in the ground state energy levels suggest the possibility of observing $\Delta|k-l| = 3$ transitions to the ν_3 band, especially for $J = 9$, where the energy level shift amounted to 0.2 cm^{-1}. A total of 9 forbidden $\Delta|k-l| = 3$ transitions can be observed from the $|J, K = 0, 0^+\rangle - |J, K = 3, 0^-\rangle$ mixing for each J value (see Fig. 1). Their intensities are weaker by a factor of $(\delta/\Delta E)^2$ compared to the intensities of the allowed transitions, where ΔE is the energy difference between the unperturbed levels that are mixed. Each of the $\Delta|k-l| = 3$ transitions would be spaced an equal distance away from the allowed transition, Δ_s, which is the energy difference between the two perturbed levels.

OBSERVED FORBIDDEN TRANSITIONS AND ANALYSIS

Table 2 lists the forbidden $\Delta|k-l| = 3$ transitions we have observed for $J = 7$, 9, and 11 of the ν_3 band, along

TABLE 2
Observed $\Delta|k-l| = 3$ Transitions in H_3O^+ and the Shifts of the Lines (Δ_s) from the Allowed $\Delta|k-l| = 0$ Transitions, in cm^{-1}

Allowed		Forbidden		Δ_s	Calculated intensity ratios
$^{r}Q(9,3)^-$	3469.262	$^{u}Q(9,0)^+$	3466.750	2.512	1/10
$^{r}P(9,3)^-$	3275.802	$^{u}P(9,0)^+$	3273.280	2.522	1/10
$^{p}P(9,3)^-$	3337.640	$^{s}P(9,0)^+$	3335.123	2.517	1/10
$^{p}Q(9,3)^-$	3529.900	$^{s}Q(9,0)^+$	3527.384	2.516	1/10
$^{r}P(9,0)^+$	3313.435	$^{o}P(9,3)^-$	3315.944[a]	2.509	1/10
$^{r}Q(9,0)^+$	3513.136	$^{o}Q(9,3)^-$	3515.651	2.515	1/10
$^{r}P(7,3)^-$	3323.231	$^{u}P(7,0)^+$	3325.884	2.653	1/69
$^{p}P(7,3)^-$	3385.075	$^{s}P(7,0)^+$	3387.725	2.650	1/69
$^{p}Q(7,3)^-$	3535.834	$^{s}Q(7,0)^+$	3538.495	2.661	1/69
$^{r}P(11,3)^-$	3327.779	$^{u}P(11,0)^+$	3220.154	7.625	1/37
$^{p}P(11,3)^-$	3290.155	$^{s}P(11,0)^+$	3282.529	7.626	1/37

[a] This transition is overlapped with another line.

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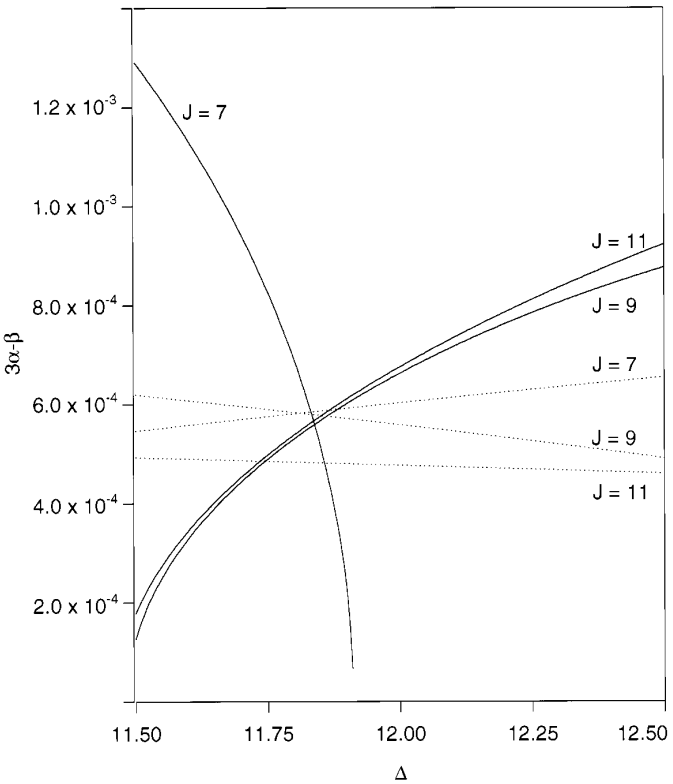

FIG. 2. Plot of Δ (in cm^{-1}) versus $3\alpha - \beta$ (in cm^{-1}) using Eq. [5] for the observed spectral splitting (solid lines) and Eq. [6] for the observed spectral shift (dashed lines) for $J = 7$, 9, and 11.

with the allowed $\Delta|k - l| = 0$ transitions for each. The superscripts u, s, and o denote $\Delta k = 4$, 2, -2, respectively. We have not obtained any *R*-branch transitions because of the difficulty of collecting spectral data in these regions due to strong H_2O absorption. Other *Q*- and *P*-branch lines not listed in Table 2 were not observed either because of the weakness of the transition or because of the interference of strong water, H_3O^+, or H_2O^+ absorption.

From the observed $\Delta|k - l| = 3$ transitions resulting from intensity borrowing from allowed transitions, an experimental value for $[C - D_{kk}K^2]$ can now be derived, which is normally undeterminable due to the $\Delta|k - l| = 0$ selection rules of symmetric tops. The mixing coefficient $(3\alpha - \beta)$ can also be obtained.

Since the perturbation appreciably mixes only two different levels which are close, their energies can be determined by solving the secular equation

$$\begin{vmatrix} E_0 - \lambda & \delta \\ \delta & E_3 + \Delta - \lambda \end{vmatrix} = 0, \qquad [4]$$

where E_0 is the energy of the $|J, K = 0, 0^+\rangle$ state from Eq. [1], and $E_3 + \Delta$ is the energy of the $|J, K = 3, 0^-\rangle$ state where the J independent term $\Delta \equiv [(0^- - 0^+) + 9(C - B) - 81D_{kk}]$ has been separated. This then gives us the solution

$$\Delta_s = \lambda_1 - \lambda_2 = [(E_0 - E_3 - \Delta)^2 + 4\delta^2]^{1/2} \qquad [5]$$

and

$$\text{shift} = \frac{1}{2}\Delta_s - \frac{E_0 - (E_3 + \Delta)}{2}, \qquad [6]$$

where shift is the difference between the observed and calculated ground state combination differences. Plots of $(3\alpha - \beta)$ versus Δ using Eqs. [5] and [6] for $J = 7$, 9, and 11 are shown in Fig. 2, where the intersection of the lines yield $(3\alpha - \beta) = 5.7 \times 10^{-4}$ cm^{-1} and $\Delta = 11.84$ cm^{-1} for H_3O^+. Equation [5] was also solved numerically using the molecular constants of Ref. (*4*) for E_0 and E_3, yielding $(3\alpha - \beta) = 5.7(2) \times 10^{-4}$ cm^{-1} and $\Delta = 11.84 \pm 0.02$ cm^{-1}.

DISCUSSION AND CONCLUSIONS

Table 3 compares our experimental values for $C''(0^-)$ and $(3\alpha - \beta)$ and those reported in Refs. (*4*) and (*6*). We have used the theoretical value of $D_{kk} = 9.267 \times 10^{-4}$ cm^{-1}

TABLE 3
Determined Constants, in cm^{-1}

	this work	Ref. [4]	Ref. [6]
C" (0^-)	6.228(2)[a]	6.42 (6)[b]	6.270
3α-β	$5.7(2)\times10^{-4}$	$6.7(10)\times10^{-4}$	

[a]averaged theoretical value of $D_{kk} = 9.267 \times 10^{-4}$ cm^{-1} from Ref. [6] has been used to separate C" and D_{kk}
[b]the error represents 1σ

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TABLE 4
Calculated Shifts of the $|J, 3, 0^-\rangle$ Levels in cm^{-1}

(J, K)	shift
7, 3	0.036
9, 3	-0.180
11, 3	-0.187

from Ref. (*6*) to separate C'' and D_{kk}. Our C'' value is different from the previous experimental value beyond the quoted uncertainty, but is closer to the theoretical value (*6*). Our $(3\alpha - \beta)$ value agrees approximately with that given in Ref. (*4*). If we use the theoretical value $\alpha = 0.836\ (200) \times 10^{-4}$ cm^{-1} given by Papoušek *et al.* (*7*), we obtain $\beta = -3.2 \times 10^{-4}$ cm^{-1}.

Table 4 lists the calculated shifts for $J = 7$, 9, and 11, which have been obtained using our experimentally determined $(3\alpha - \beta)$. The values agree well with the observed shifts listed in Table 1 for the $J = 7$ and 9 levels. For the $J = 11$ level shift, they differ by 0.046 cm^{-1}, indicating that the energy expression of Eq. [1] is not sufficient for high J levels. We believe that the major cause of this discrepancy is the A_1–A_2 splitting of $K = 3$ levels with the form

$$(-1)^J h_3 (J + 3)!/(J - 3)!. \qquad [7]$$

The drastic J^6 dependence makes this effect negligible for low J values but significant for $J = 11$. If this interaction is included, we obtain $h_3 = 0.59\ (12) \times 10^{-10}$ cm^{-1}. The inclusion of the h_3 term also moves the $J = 11$ shift line closer to the other lines in Fig. 2. However, since our determination of h_3 is dependent effectively on only a few transitions, the value of h_3 may not be accurate.

In conclusion, we have observed 11 $\Delta|k - l| = 3$ transitions in the ν_3 band of H_3O^+. These transitions have enabled us to obtain values for the C rotational constant for the antisymmetric ground state and an off-diagonal centrifugal distortion constant. A natural extension of this work would be to find the $\Delta k = 3$ transitions in the far infrared rotation–inversion spectrum and in the ν_2 inversion band. They will appear at positions shifted by the same amount and with the same relative intensities with respect to the allowed transitions as listed in Table 2.

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