Infrared spectrum of the fundamental vibration–rotation band of OD⁻

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The fundamental $v = 1 \leftarrow 0$ vibration–rotation band of OD⁻ has been observed using the tunable infrared radiation from a difference frequency laser system and the velocity modulation technique for detection. The band origin is determined to be 2625.332(3) cm⁻¹. The rotational constant B and the centrifugal distortion constant D have been determined for both the ground state and the first excited state. A remarkable similarity between molecular constants of OD⁻ and OD has been noticed and utilized to estimate equilibrium vibration–rotation constants. These vibration–rotation constants were used to estimate the equilibrium bond length and the quadratic, cubic, and quartic force constants.

I. INTRODUCTION

In the last several years, high resolution infrared spectroscopy of molecular ions using glow discharges has made remarkable progress. Using various techniques of laser systems and discharges, spectra of ions with concentrations on the order of 10^8 cm⁻³ are now detectable. Anions are a challenge to molecular spectroscopists because their concentration in glow discharges is lower than that of cations typically by two orders of magnitude. Until very recently, the only spectral data on these species were derived from low resolution photodetachment studies and solid state work.[1] Recently, very high resolution photodetachment studies of OH⁻ and OD⁻ by Schulz, Mead, Jones, and Lineberger[2] has given accurate rotational constants of these ions in the ground state. Similar methods were used[3,4] to study high resolution spectra of NH⁻, CH₂CN⁻, and CH₂CO⁻. On the other hand, the progress in the *ab initio* calculation of simple molecular ions has enabled theoreticians to predict accurate molecular structures, dipole-moment functions and vibrational frequencies of negative ions.[5,6]

Very recently, Owrutsky, Rosenbaum, Tack, and Saykally[7] have observed the vibration–rotation spectrum of OH⁻ in the 2.8 μm region and Liu and Oka[8] have observed the pure rotational spectrum in the 25 and 27 μm regions. These studies together with that of Schulz *et al.* have revealed that the vibrational and rotational constants of OH⁻ are remarkably close to those of the OH radical.[9] This led us to believe that the OD⁻ constants would be similar to those of the OD radical,[10] thus piquing our interest in obtaining the equilibrium vibration–rotation constants for this molecular ion.

II. EXPERIMENTAL

A difference frequency laser system[11] was used to generate tunable infrared radiation. An 80×1.2 cm i.d. water-cooled ac discharge cell was used to produce the OD⁻ ion. In order to increase the sensitivity, the infrared was passed through the cell four times unidirectionally and noise subtraction[12] was used to reduce the infrared laser source noise. The velocity modulation technique of Gudeman, Begemann, Pfaff, and Saykally[13] was employed to discriminate the ion lines from the much stronger neutral lines. Initially a gas mixture of D₂ and O₂ in a 3:1 ratio with a total pressure of 1

Torr was used, but a large number of absorption lines from neutral species were observed, obscuring much of the spectrum. We then changed to a gas mixture of D₂ and O₂ in a 1:3 ratio. This suppressed many of the neutral absorption features and increased the OD⁻ signals. The density of these neutral absorption lines probably caused by D₂O, OD, and others indicate the complexity of the discharge chemistry even in a simple two component mixture.

III. OBSERVED SPECTRUM

The absorption lines of OD⁻ observed between 2400 and 2800 cm⁻¹ are listed in Table I. Figure 1 shows the $1f$ absorption signal of the R(5) transition of OD⁻ as an example. The top trace is the spectrum of H₂CO, which was used as a frequency standard[14] along with N₂O, D₂O, and HDO. Velocity modulation is useful not only for suppressing the neutral absorptions, but also for discriminating negative and positive ion signals by their phase.

The observed OH⁻ band origin[7] properly scaled was

TABLE I. Observed frequencies of $1 \leftarrow 0$ band of OD⁻.

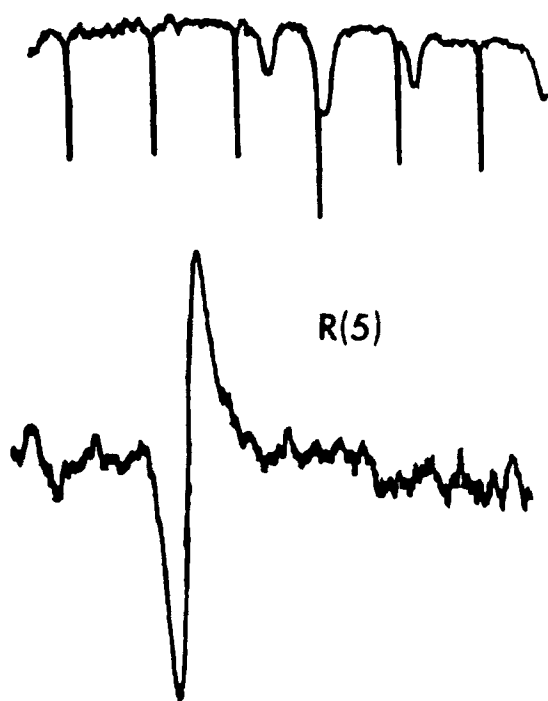| Assignment	Frequency (cm⁻¹)	Obs − calc × 10³
P(1)	2605.363	− 2
P(2)	2584.815	0
P(3)	2563.693	− 1
P(4)	2542.016	− 1
P(5)	2519.800	2
P(6)	2497.050	0
P(7)	2473.787	0
P(9)	2425.790	a
P(10)	2401.052	0
R(0)	2644.706	3
R(1)	2663.462	0
R(2)	2681.600	0
R(3)	2699.102	1
R(4)	2715.953	− 2
R(5)	2732.146	0
R(6)	2747.665	0
R(7)	2762.499	0
R(8)	2776.634	0
R(9)	2790.060	1
R(10)	2802.762	0

ª Not included in the fit.

FIG. 1. The $1f$ absorption signal of the $R(5)$ transition of OD⁻. The top trace is a portion of the H_2CO spectrum which is used as a frequency reference.

used for the search of the OD⁻ spectrum. A total of 20 transitions were measured with a precision of 0.003 cm⁻¹ for the OD⁻ fundamental up to $J = 10$ in both the R and the P branches. The $P(8)$ transition was not seen due to lower infrared power in that region of the spectrum. The spectrum is fit to the usual linear molecule vibration–rotation energy expression with a least squares algorithm. H_0 and H_1 were constrained in the fit to the value of H_e of the OD radical[10] due to the remarkable similarity between the molecular constants of OD and OD⁻. The determined molecular constants are shown in Table II together with those of OD for comparison.

IV. EQUILIBRIUM MOLECULAR CONSTANTS

Since we have observed only the fundamental band $v = 1 \leftarrow 0$ of OD⁻ we need additional information for esti-

TABLE II. Molecular constants for the $1 \leftarrow 0$ band of OD⁻ and OD[10] (cm⁻¹).

	OD⁻	OD
	$v_0 = 2625.332(3)^a$	$v_0 = 2632.105(9)$
	$B_0 = 9.984\ 59(21)$	$B_0 = 9.883\ 00\ (13)$
	$B_1 = 9.686\ 15(19)$	$B_1 = 9.607\ 10(15)$
	$D_0 = 5.549(15) \times 10^{-4}$	$D_0 = 5.3825(33) \times 10^{-4}$
	$D_1 = 5.470(12) \times 10^{-4}$	$D_1 = 5.2978(36) \times 10^{-4}$
	$H_0 = H_1 = 2.056 \times 10^{-8\ b}$	$H_0 = 2.015(33) \times 10^{-8}$
		$H_1 = 1.932(23) \times 10^{-8}$

[a] Numbers in parentheses are 3σ.
[b] OD⁻ molecular constants determined with $H_0 = H_1 = 2.056 \times 10^{-8}$ as a constraint.

mating some of the equilibrium vibration and rotation constants. This extra information is obtained from the constants of OH⁻ determined by Owrutsky et al.[7] and from the constants of OD and OH determined by Amiot, Maillard, and Chauville[10] and Maillard, Chauville, and Mantz,[9] respectively. The similarity between the molecular constants of OD⁻ and OD indicate that the added electron on OD⁻ does not appreciably alter the bond length or the bond strength of the OD molecule. Since very extensive observation and analysis have been carried out for OH and OD using the hot bands (up to $v = 5 \leftarrow 4$) to determine many of the equilibrium constants, we can use the relationship between these constants as added constraints to determine the equilibrium constants of OD⁻. Our procedure for estimating the constants is as follows.

A. Rotational constants and equilibrium structure

From the observed rotational constants B_0 and B_1, we calculate B_e and α_e using the following formula:

$$B_v = B_e - \alpha_e (v + \tfrac{1}{2}) + \gamma_e (v + \tfrac{1}{2})^2 . \tag{1}$$

Since this equation has three independent parameters we use α_e and γ_e of OD as added information. From the observed value of B_0 and B_1 listed in Table II, we notice that although the values of B are very close, the values of α are significantly different. The following iteration procedure was used to estimate B_e, α_e, and γ_e of OD⁻. We first neglected γ_e of OD⁻ and calculated the first set of B_e and α_e. The value of B_e thus obtained is very close to that of OD and α_e slightly different. We next used γ_e(OD) $[\alpha_e(\text{OD}^-)/\alpha_e(\text{OD})]^2$ as the γ_e value for OD⁻ and calculated the second set of B_e and α_e. This was repeated until convergence to obtain the final B_e, α_e, and γ_e values. The equilibrium centrifugal distortion constants were determined from the observed D_1 and D_0 using the formula

$$D_v = D_e - \beta_e (v + \tfrac{1}{2}) . \tag{2}$$

TABLE III. Estimated equilibrium molecular constants for OD⁻ compared with those of OD.[a,b,c]

	OD⁻	OD
B_e	10.135 99(30)	10.0225
α_e	0.304 3(5)	0.2802
γ_e	$0.292(20) \times 10^{-2}$	0.2475×10^{-2}
D_e	$5.588(18) \times 10^{-4}$	5.4273×10^{-4}
β_e	$0.079(19) \times 10^{-4}$	0.0929×10^{-4}
ω_e	2723.5(10)	2721.85
$\omega_e x_e$	49.72(50)	45.34
$\omega_e y_e$	0.38(15)	0.32
f_2	2723.5	2721.85
f_3	− 1652.6	− 1587.46
f_4	875.7	817.59
F_2	7.82 mdyn/Å	7.81 mdyn/Å
F_3	− 57.0 mdyn/Å²	− 54.8 mdyn/Å²
F_4	364 mdyn/Å³	339 mdyn/Å³
r_e	0.964 24(8) Å	0.969 67 Å

[a] All values are in cm⁻¹ except for r_e and F_n.
[b] Values in parentheses are 3σ.
[c] All OD data taken from Ref. 10.

The equilibrium bond length of OD⁻ was determined from B_e. All the estimated equilibrium values are listed in Table III.

B. Vibrational constants

The estimation of the equilibrium vibrational constants was more difficult because we have only one observed value. It was necessary therefore to add the OH⁻ band origin reported by Owrutsky et al. as well as OH and OD data for initial guesses of $\omega_e y_e$ for OH⁻ and OD⁻, respectively, to calculate the three unknown parameters in the vibrational formula

$$\omega_v = \omega_e - \omega_e x_e (v + \tfrac{1}{2}) + \omega_e y_e (v + \tfrac{1}{2})^2 . \qquad (3)$$

We assume that the equilibrium constants scale between isotopic species as expected from the usual reduced mass ratio; this is equivalent to neglecting the Δ values in the formula for the breakdown of the Born–Oppenheimer approximation.[15] It is indeed found between OH and OD that this approximation is accurate for ω_e to within 3×10^{-4} and $\omega_e x_e$ to within 7×10^{-3}. So we proceed as follows. We first assume the values of $\omega_e y_e$ for OH and OD to be those of OH⁻ and OD⁻, respectively. Then we determine the values of ω_e and $\omega_e x_e$ for OH⁻ and OD⁻ using the mass scaling $\mu^{-1/2}$ and μ^{-1} where μ is the reduced mass. The value of $\omega_e y_e$ is assumed to be $\omega_e y_e (\mathrm{OX})[\omega_e x_e (\mathrm{OX}^-)/\omega_e x_e (\mathrm{OX})]^2$, where X = H,D for OH⁻ and OD⁻, respectively. The converged values of ω_e, $\omega_e x_e$, and $\omega_e y_e$ of OD⁻ are listed in Table III.

C. Potential constants

From the equilibrium molecular constants ω_e, α_e, and $\omega_e x_e$ we can calculate the vibrational potential defined in terms of the dimensionless normal coordinate q as follows:

$$\frac{V(q)}{hc} = \frac{1}{2!} f_2 q^2 + \frac{1}{3!} f_3 q^3 + \frac{1}{4!} f_4 q^4 + \cdots , \qquad (4)$$

where f_2, f_3, and f_4 are the quadratic, cubic, and quartic potential constants in wave numbers. After a perturbation treatment[16] we find that these potential constants are expressed in terms of B_e, α_e, ω_e, and $\omega_e x_e$ as follows:

$$f_2 = \omega_e , \qquad (5)$$

$$f_3 = -\left[\alpha_e + \frac{6 B_e^2}{\omega_e} \right] \left[\frac{\omega_e^3}{2 B_e^3} \right]^{1/2} , \qquad (6)$$

and

$$f_4 = -16 \omega_e x_e + \frac{5}{3} \frac{f_3^2}{\omega_e} , \qquad (7)$$

these potential constants are converted to the conventional force constants F_2, F_3, and F_4 in the vibrational potential defined as

$$V(r) = \frac{1}{2!} F_2 r^2 + \frac{1}{3!} F_3 r^3 + \frac{1}{4!} F_4 r^4 + \cdots \qquad (8)$$

by noting that

$$q = 2\pi \sqrt{\frac{\omega_e c \mu}{h}} \, r , \qquad (9)$$

where μ is the reduced mass. Thus

$$F_n = hc \left(2\pi \sqrt{\frac{\omega_e c \mu}{h}} \right)^n f_n . \qquad (10)$$

The force constants, F_n, are easier to interpret physically and are isotope independent while f_n are convenient in that the relations with molecular constants Eqs. (5)–(7) are simpler and that they show the order of magnitude of each potential term more clearly. The calculated values of f_n and F_n for $n = 2$–4 are listed in Table III.

The values of f_n show rather clearly that the potential terms in Eq. (4) do not converge rapidly for hydrides even if we consider the $n!$ factor in the denominator, though the convergence of the experimental vibration–rotation constants ω_e, $\omega_e x_e$, $\omega_e y_e$, and B_e, α_e, γ_e is excellent. This suggests that contributions from a higher order perturbation treatment is sizable. Indeed if we carry out higher order treatment[17] for $\omega_e x_e$ for example, we find that the terms from f_3^2 and f_4, which appear in Eq. (7) as the principal terms (of the order of magnitude λ^2) of the perturbation treatment, are only one order of magnitude greater than the next terms (of the order of magnitude λ^6) from f_4^3, $f_4^2 f_3^2$, $f_4 f_3^4$, and f_3^6, etc. Thus the value of f_2, f_3, and f_4, especially the last one, contains sizable error due to the neglect of higher order terms. The RKR treatment may be more useful especially for calculating higher order vibrational terms.

V. DISCUSSION

The similarity between the OH and OH⁻ bonds has earlier been mentioned by Schulz et al.[2] Our results given in Table III make this point even more striking. The equilibrium bond length r_e, the harmonic vibrational frequency ω_e, and thus the quadratic force constants F_2 are nearly identical (to within 0.5%) between OD and OD⁻. The electron added to OH completes the nonbonding $(1\pi_y)^2$ orbital, but does not make the chemical bond any stronger. This situation is quite different from the case of OH⁺ and OH for which the added electron [which pairs with one of the two unpaired nonbonding electrons, thus completing the $(1\pi_x)^2$ nonbonding orbitals] significantly shortens the bond r_e (1.0289→0.9697 Å) and increases the vibrational frequency ω_e (3113→3738 cm⁻¹).[18] For the case of HF⁺ and HF which are isoelectronic to OH and OH⁻, the variation is also very pronounced; r_e (1.0011→0.9168 Å) and ω_e (3090→4138 cm⁻¹). It seems that adding an electron to a cation alters the structure yet adding an electron to the neutral species does not change the structure.

The molecular constants such as α_e and $\omega_e x_e$ which contain contributions from the anharmonic terms of the potential differ more between OD and OD⁻ ($\sim 10\%$). This leads to the different anharmonic force constants. All these results are difficult to explain qualitatively but the detailed theoretical results of Weiner, Rosmus, and Reinsch are in agreement with our experimental results.

We can also look at OH⁻ as deprotonated H_2O. It is interesting to note that the O–H bond length does not vary much from H_2O (0.958 Å)[19] to OH⁻ (0.964 Å). The force constants of OD⁻ ($F_2 = 7.82$ mdyn/Å, $F_3 = -57.0$ mdyn/Å², and $F_4 = 364$ mdyn/Å³) are also close to those of

H_2O ($F_2 = 8.45$ mdyn/Å, $F_3 = -59.4$ mdyn/Å^2, and $F_4 = 384$ mdyn/Å^3).[19]

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