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$$\gamma(r) = 6a^2/r^3 - \lambda \exp(-r/r_0), \quad (2)$$

with $\lambda = 42.5$ a.u. and $1/r_0 = 1.645$ a.u., at zero frequencies. Using that model and the dc atomic polarizability, we obtain curve 2 of Fig. 1, which is generally a somewhat poorer fit of the data. However, if we use $a = 1.40$ a.u. instead of the dc value, the approximation is improved (curve 3). (No frequency dependence is known for λ, r_0 .)

We mention that Eq. (2) was derived with electron correlation neglected. Correlation corrections of the atomic polarizability are known to be of the same order as the incremental pair polarizabilities. Hence, correlation is likely to affect the anisotropy.⁷ Our results presented in Fig. 1 suggest that the effect of correlation is to decrease the term $\lambda \exp(-r/r_0)$. For example, if we use a λ value of 14 a.u. instead of 42.5 a.u. (and $a = 1.40$ a.u.; $1/r_0 = 1.645$ a.u.), the resulting curve 4 is a near perfect fit of the experimental data. Corrections of this magnitude are not likely due to frequency alone; correlation appears to be essential.

It is interesting to look in conclusion at similar results for other gases. Our previous work⁸ showed that the DID model provides an amazingly accurate ($\pm 5\%$) approximation of the true anisotropy of argon, krypton, xenon, and methane, just as this was seen above for the case of helium. The more sophisticated Hartree-Fock calculation⁷ for He₂ appears to correct the DID

model in the right direction, but overcorrects it several times. New calculations of the pair polarizabilities should include correlation and nonzero frequencies.

While completing our work, a measurement of the collision-induced helium spectrum appeared.⁹ Much higher pressures and a different calibration method were used. The experimental results are not in complete agreement with our work.

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The reaction of hydrogen atoms with ozone: Evidence for a second reaction path producing HO₂ and O(³P)^a

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The reaction of hydrogen atoms with ozone is important in chemical dynamics,¹ in the chemistry of the upper atmosphere,² and as a source of vibrationally excited hydroxyl radicals, OH(²π_i)_{v<9}, (OH[†]).³⁻⁵ As part of our studies of the kinetics of the reactions of vibrationally excited OH, it became essential to redetermine the rate constant and net reactant stoichiometry ($\Delta[\text{O}_3]/\Delta[\text{H}]$) of this reaction. However, not being able to obtain a quantitative interpretation of our data using only reaction (1) followed by known secondary reactions of the product OH[†], we were led to consider the possibility of a second primary process, Reaction (2):

We report here experimental evidence for (2), obtained directly by monitoring the yield of O(³P) and indirectly by measuring ground state OH concentrations produced from known concentrations of H and O₃.

Hydrogen atoms were produced in a conventional fast-flow discharge system operated at 299 ± 2 °K and 1.1 ± 0.1 Torr total pressure with argon as the bath gas. Initial concentrations were determined by titration with NO₂ and following either the loss of H or the increase in ground state OH.⁶ Mixtures of O₃ in helium, whose concentrations were determined by the absorbance at 253.7 nm, were then added through a movable inlet.

Both O(³P) and ground state OH were measured as a function of reaction time using the resonance fluorescence technique at a fixed port at the downstream end of the flow tube. The net emission from the atomic oxygen lines at 130.2, 130.5, and 130.6 nm was measured perpendicular to the direction of the exciting radiation using an evacuated monochromator and a solar blind photomultiplier. The resonance fluorescence intensity from OH was measured at the same port using a 309.5 ± 2.8 nm interference filter and cooled photomultiplier.⁶ Calibration of the system to convert the

observed intensities to absolute concentrations of $O(^3P)$ or OH, respectively, was carried out by adding either small measured amounts of $NO(<10^{12} \text{ cm}^{-3})$ to a stream of nitrogen atoms ($>5 \times 10^{12} \text{ cm}^{-3}$) to form $O(^3P)$, or by adding $NO_2 (<6 \times 10^{11} \text{ cm}^{-3})$ to hydrogen atoms ($\geq 10^{12} \text{ cm}^{-3}$) to form OH. Observation times were sufficiently long (45 msec) that these reactions were complete.

Since no loss of $O(^3P)$ at the halocarbon wax coated walls was observed in the $N+NO$ system, the initial concentration of NO was equal to the concentration of $O(^3P)$ at the detection port. The concentrations of OH produced from the $H+NO_2$ reaction were calculated from the initial NO_2 concentrations; corrections were applied for the first order wall loss ($k_w = 4\text{--}12 \text{ sec}^{-1}$) which was measured before and after each set of experiments, and for a small loss due to the bimolecular reaction of OH at the highest NO_2 concentrations used.

The ranges of initial hydrogen atom and ozone concentrations were $(1\text{--}3) \times 10^{12} \text{ cm}^{-3}$ and $(3\text{--}7) \times 10^{11} \text{ cm}^{-3}$, respectively. In all cases hydrogen atoms were kept in excess ($[H]_0 \geq 4 [O_3]_0$) to deactivate the $OH^\dagger$, a process which occurs essentially on every collision.^{5,7}

In the first series of experiments $O(^3P)$ was not only detected but also found to be a significant product. For example, with $[H]_0 = 1.8 \times 10^{12} \text{ cm}^{-3}$ and $[O_3]_0 = 4.2 \times 10^{11} \text{ cm}^{-3}$, its peak concentration was $1.0 \times 10^{11} \text{ cm}^{-3}$. Under these conditions, where deactivation of $OH^\dagger$ is almost entirely by atomic hydrogen, there are three possible secondary sources of $O(^3P)$ in addition to primary process (2): (a) reaction of OH with OH (each with or without vibrational excitation), (b) reaction of $OH^\dagger$ with H, and (c) reaction of HO_2 with H.

Process (a) can be excluded immediately since the observed concentrations of $O(^3P)$ were three times those expected under the "worst case" assumption that the rate constant⁸ for the bimolecular reaction of OH increases from 1.7×10^{-12} to $4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ if at least one of the OH radicals is vibrationally excited. To test (b), large concentrations of $CO_2 (1 \times 10^{15} \text{ cm}^{-3})$ or $O_2 (8 \times 10^{14} \text{ cm}^{-3})$ were added; both of these molecules deactivate $OH^\dagger$ rapidly with rate constants^{5,9} of 6×10^{-12} and $3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, respectively. On the basis of current theories of energy transfer, it is reasonable to assume that they also deactivate the lower vibrational levels ($v' = 1\text{--}8$) with comparable (order-of-magnitude) efficiency. Thus, in these experiments $OH^\dagger$ should be deactivated primarily by CO_2 or O_2 , rather than H, and a drop in the $O(^3P)$ concentration is expected if it is being produced by the reaction of $OH^\dagger$ with H; in fact, no change ($<2\%$) in the $O(^3P)$ was observed. This is consistent with the studies of Glass *et al.*⁷ in which the removal of $OH^\dagger_{v',1,2}$ by H was shown to proceed predominantly by deactivation rather than reaction.

The reaction of H with HO_2 , possibility (c), has three reaction channels: They produce $H_2 + O_2$ (0.51), $2OH$ (0.26), or $H_2O + O$ (0.23), respectively, where the branching ratios¹⁰ are given in parentheses. The low fraction of this reaction leading to $O(^3P)$ implies that this can only be an important source of $O(^3P)$ if there is

a significant source of HO_2 . Without Reaction (2), the only source of HO_2 is the reaction of $OH^\dagger$ with O_3 . Since vibrationally excited OH is deactivated primarily by H and the reaction of ground state OH with O_3 is slow ($k = 5.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$),¹¹ the concentrations of HO_2 so produced would be too small to account for the observed $O(^3P)$ concentrations. (This is true even if one assumes $OH^\dagger$ reacts with O_3 on every collision to produce HO_2).

Since known secondary reactions cannot produce the observed concentrations of $O(^3P)$, primary process (2) is the logical source of $O(^3P)$ and HO_2 . To obtain quantitative estimates of the relative importance of (2), a reaction scheme consisting of (1) and (2) followed by known secondary reactions of the $OH^\dagger$, HO_2 , $O(^3P)$, etc., was constructed and numerical integration of the differential equations governing the concentration of each species was carried out; details of the reaction scheme and procedure will be discussed elsewhere.¹² The branching ratio between (1) and (2) was varied to obtain a best fit to the observed $O(^3P)$ concentrations in each run. Good fits were obtained for all runs if $\sim 20\%$ to 30% of the net reaction was assumed to proceed via (2).

In the second set of experiments concentrations of ground state OH were measured; this species is produced upon deactivation by hydrogen atoms of the $OH^\dagger$ formed in (1). Although this is a less sensitive measure of the extent of Reaction (2), and inherently has larger errors associated with it, nevertheless the observed OH concentrations were significantly lower than those predicted if only primary process (1) occurs. For example, with $[H]_0 = 3.0 \times 10^{12} \text{ cm}^{-3}$, $[O_3]_0 = 6.9 \times 10^{11} \text{ cm}^{-3}$, and $k_w = 12 \text{ sec}^{-1}$, the peak concentration of OH was $2.7 \times 10^{11} \text{ cm}^{-3}$, which is $\sim 70\%$ of that anticipated if (2) does not occur. Addition of high concentrations ($1 \times 10^{15} \text{ cm}^{-3}$) of CO_2 did not significantly change the yield of ground state OH, indicating again that reaction of $OH^\dagger$ with H is not a significant loss process for $OH^\dagger$. The results of these experiments also indicate that $\sim 20\%$ – 30% of the reaction gives $HO_2 + O(^3P)$.

In conclusion, the results of these experiments indicate that unless there are as yet unrecognized secondary reactions which remove OH and produce $O(^3P)$, an alternate path in the reaction of hydrogen atoms with ozone to produce HO_2 and $O(^3P)$ accounts for $\sim 20\%$ – 30% of the net reaction. Experiments are planned to measure the HO_2 yield to confirm these results. The implications of this work for the chemistry of the stratosphere and mesosphere will be discussed more fully in a future publication.¹²

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A spectrum of triatomic hydrogen

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Two examples of Rydberg spectra of diatomic molecules that are unstable in their ground states are known: He_2 , known since the early days of molecular spectroscopy,¹ and ArH , more recently discovered by Johns.² The Rydberg states responsible for these spectra are stable, bound states since the core, He_2^+ , and ArH^+ , respectively, is stable.

In this Communication I wish to report the observation of the Rydberg spectrum of an unstable *polyatomic* molecule, namely discrete spectra of triatomic hydrogen (H_3 and D_3).

The spectra under discussion were first observed in an ordinary hollow cathode discharge tube through H_2 or D_2 at a pressure of about 1 Torr. It is greatly strengthened when the cathode is cooled to liquid nitrogen temperature but does not occur in the positive column of the same discharge (it has then less than $\frac{1}{10}$ the intensity of that observed in the hollow cathode).¹⁰ The main features of the new spectrum (in both H_2 and D_2) are two fairly strong emission bands near 5600 and 7100 Å each consisting of rather broad (diffuse) lines. The widths of

the lines are considerably reduced when going from H_2 to D_2 . This behavior is very similar to that observed for ArH and also to that observed for many absorption spectra of diatomic and polyatomic hydride molecules.

The band observed for D_2 near 5600 Å is shown in Fig. 1. It has a well resolved *P* and *R* branch and a partly resolved *Q* branch. The first idea about the nature of the spectrum was that it represents a new transition of H_2 or D_2 with a predissociating lower state. There is indeed a strong predissociation observed in H_2 in this same region.³ However when the *B* values for the upper and lower state were determined (a very simple and unambiguous matter since the band is so simple) the values $B' = 22.4_3$, $B'' = 23.0_9 \text{ cm}^{-1}$ were found. All observed excited states of D_2 have *B* values of less than 16 cm^{-1} in accordance with the fact that most of them are Rydberg states whose *B* values are expected to be similar to that of the D_2^+ ion for which B_0 is 14.74 cm^{-1} . Doubly excited non-Rydberg states have much smaller *B* values. There is no possibility that any predicted (and not yet observed) states could have *B* values larger

FIG. 1. 5600 Å band of D_3 . Two spectra of different exposure time of a hollow cathode discharge in D_2 at liquid nitrogen temperature are shown. The many sharp lines are due to D_2 .