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Effects of rotational, vibrational, and translational energy on the rate constants for the isotope exchange reactions $OH^- + D_2$ and $OD^- + H_2$

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Rate constants for the isotope exchange reactions of OH^- with D_2 and OD^- with H_2 have been measured as a function of average center-of-mass kinetic energy at several temperatures. The reaction of OH^- with D_2 is slightly exothermic, and the rate constant has a negative temperature dependence. The kinetic energy dependences of the rate constants have minima near 0.1 eV. A strong negative dependence on the D_2 rotational temperature was found. The reason for this dependence is unclear at present. In contrast, the reaction of OD^- with H_2 is slightly endothermic and shows positive dependences on both temperature and kinetic energy. The negative rotational dependence for the reaction of OD^- with H_2 is not as large as that for $OH^- + D_2$, presumably because rotational energy can help overcome the endothermicity in the case of $OD^- + H_2$. Vibrational energy is observed to promote reactivity in both reactions.

INTRODUCTION

We have developed a technique that allows for determination of the effect of internal energy on reactivity of ion–molecule reactions.[1,2] When the vibrational frequencies of the reactants are large, we can determine rotational temperature dependences. We have studied a number of systems involving monatomic ions, the case for which the data are most easily interpreted.[1-7] For polyatomic ions, it is usually not possible to separate the effects of reactant ion and reactant neutral internal energy. An exception is when the masses of the reactant neutral and the helium buffer are equal. Our technique is most sensitive for reactions whose rate constants are in the range from 10^{-10} to 10^{-11} $cm^3\,s^{-1}$. A reaction which fits these criteria is the isotope exchange reaction of OH^- with D_2,

$$OH^- + D_2 \rightarrow OD^- + HD,\quad \Delta H = -1.8\,\mathrm{kJ\,mol^{-1}}\ \text{(Ref. 8)}. \tag{1}$$

In this paper, we report the rate constants for this reaction as a function of average ion-neutral center-of-mass kinetic energy $\langle KE_{c.m.}\rangle$ at several temperatures, and from these data we derive the dependence of the rate constants on the rotational temperature of D_2. We also report data on the related reaction

$$OD^- + H_2 \rightarrow OH^- + HD,\quad \Delta H = +2.5\,\mathrm{kJ\,mol^{-1}}\ \text{(Ref. 8)}. \tag{2}$$

The thermicities reported here for reactions (1) and (2) are based on vibrational zero-point energies[8] and differ by only 0.1 to 0.2 kJ mol^{-1} from the values obtained from heats of formation.[9]

In addition, it was possible to vibrationally excite the OH^- and OD^- reactants, and we report rate constants for $OH(D)^-(v>0)$. We believe that these results, along with our recent work on the charge transfer reaction of O_2^- with SF_6, represent the first rate constants for vibrationally excited negative ions.[10]

EXPERIMENT

The measurements were made using the Phillips Laboratory variable temperature-selected ion flow drift tube apparatus.[5] Instruments of this type have been the subject of review,[11] and only those aspects important to the present study will be discussed in detail. $OH(D)^-$ ions were created by electron impact on $H(D)_2O$ in a moderate pressure ion source (~0.1 Torr). The ions were extracted from the source and mass selected in a quadrupole mass filter and injected into a flow tube 1 m in length through an orifice of 2 mm diameter. Helium buffer gas transported the ions along the length of the flow tube. The pressure in the flow tube was ~0.4 Torr. A drift tube is positioned inside the flow tube for studies of $\langle KE_{c.m.}\rangle$ dependences. A small fraction of the ions in the flow tube was sampled through a 0.2 mm hole in a sampling nose cone, mass analyzed in a second quadrupole mass spectrometer, and detected by a channel electron multiplier.

The H_2 or D_2 neutral reactant gas was added through one of two inlets, and rate constants were determined from the decay of the primary ion signal as a function of the neutral flow rate. The ion velocity and therefore the reaction time were determined by conse[illegible] drift rings and acquiring the arrival time spectra. The entire flow tube could be heated or cooled, in this case over the range 129 to 508 K. All parameters including ion velocity and the end correction were measured for each rate constant determination. The accuracy of the measurements is estimated to be 25%, and the accuracy of each point relative to the others (relative error) is estimated to be 15%.[5]

In order to understand the data, one must bear in mind the various energy and temperature distributions in a nonthermal drift tube experiment: (1) The average kinetic energy in the ion-neutral center-of-mass system $\langle KE_{c.m.}\rangle$ in the drift tube is derived from the Wannier formula[12] as

$$\langle KE_{c.m.}\rangle = \frac{(m_i+m_b)m_n}{2(m_i+m_n)}\,v_d^2 + \frac{3}{2}kT, \tag{3}$$

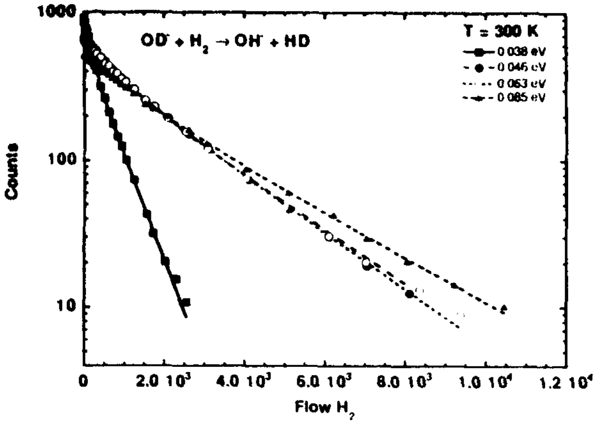

FIG. 1. Semilogarithmic decay of OD$^-$ signal as a function of H_2 flow rate at 300 K for several values of average kinetic energy, $\langle KE_{c.m.}\rangle$. The lines are fits to double exponential decays.

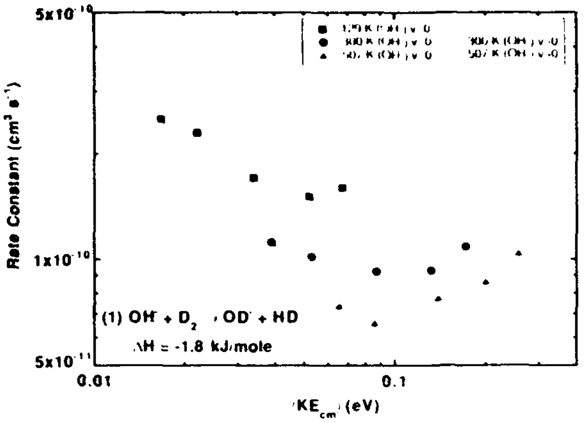

FIG. 2. Rate constants for the isotope exchange reaction of OH$^-$ with D_2 as a function of average kinetic energy, $\langle KE_{c.m.}\rangle$, at several temperatures. Data obtained with no added drift field are connected by a solid line (pure temperature dependence). Solid symbols refer to ground-state OH$^-$, and open symbols of the same shape refer to vibrationally excited OH$^-$ at the same temperatures.

where m_i, m_b, and m_n are the masses of the reactant ion, buffer gas, and reactant neutral, respectively; v_d is the measured ion drift velocity; and T is the temperature. The first term in the formula is the energy supplied by the drift field, and the second term is the thermal energy. (2) The neutral reactant internal temperature is the same as that of the buffer gas. (3) The effective internal temperature of the OH(D)$^-$ is also derived from the Wannier expression by substituting the buffer mass for the reactant neutral mass, and $\langle KE_{c.m.}\rangle_{buf}=(3/2)kT_{int}$. Due to the high vibrational frequencies of the ions in this study there is no thermal vibrational excitation. However, as will be shown below, we can choose conditions where the OH(D)$^-$ ions are created with vibrational energy. Under conditions where the ions are injected into the flow tube at relatively high energy (~ 100 V), about 30% of the ions are vibrationally excited. This is comparable to the fraction of vibrationally excited positive ions typically formed by this technique in our apparatus.

RESULTS AND DISCUSSION

Under conditions where OH(D)$^-$ was injected into the flow tube at low energy, plots of the logarithm of OH(D)$^-$ vs D(H)$_2$ flow rate were linear, as is usual when only one state of the ion is present. However, when OH(D)$^-$ was injected at energies of about 100 eV the decay was not linear indicating the presence of more than one state.[13] Figure 1 shows the decay of OD$^-$ as a function of H_2 flow rate at 300 K for several values of $\langle KE_{c.m.}\rangle$ (several applied electric field strengths). In all cases, the decays are nonlinear indicating the presence of two or more vibrational levels. The excitation must be vibrational and not electronic since OH(D)$^-$ is a closed-shell species and therefore has no low-lying electronic states. The lines are fits to double exponential decays, a treatment which assumes that two states of OD$^-$ are present and react at different rates with H_2. Evidence that the curvature is due to excited states and not some other cause is twofold: (1) the curvature was not observed upon addition of SF_6 upstream of the reaction region, which presumably quenched the OH(D)$^-$ excited state, and (2) the curvature only occurred when the OH(D)$^-$ was injected into the flow tube at high energy. Vibrational excitation of diatomic positive ions upon high injection energy is common in our apparatus.[13-15] However, this along with recent data from our laboratory on the reaction of vibrationally excited O_2^- reacting with SF_6 are the first data indicating that this technique works for negative ions as well.

Rate constants for the excited states are determined from the double exponential fits to the curved decays. The ratio of the exponential factors is equal to the ratio of the rate constants. The slower decay matches the single, linear decay under conditions where no vibrational excitation is present, and therefore the faster decay is due to the vibrationally excited OH(D)$^-$. It should be noted that the fast decay corresponds to both reaction and vibrational quenching. While the data show that vibrational excitation increases the rate constant, the apparatus does not have the diagnostic capability at present for determining which state(s) is responsible for the enhancement in reactivity or whether there are more than two decays in the data. We estimate that the rate constants for vibrationally excited OH(D)$^-$ are accurate to within approximately a factor of 2.

Figures 2 and 3 show the rate constants for reactions (1) and (2), respectively, as a function of $\langle KE_{c.m.}\rangle$ at different temperatures. To aid in looking at the data all points for ground-state reactant ions are shown as solid symbols and the data for vibrationally excited reactant ions are shown as open symbols. In the case of the OD$^-$ reactant ion, we observed curvature, and therefore we additionally measured rate constants for vibrationally excited OD$^-$ for most temperatures and kinetic energies. However, for the OH$^-$ reactant, curvature was only observable under a minimum number of conditions, and less data were obtained for vibrationally excited OH$^-$. This may be due to the ratio of fast ($v>0$) to slow ($v=0$) rates being larger

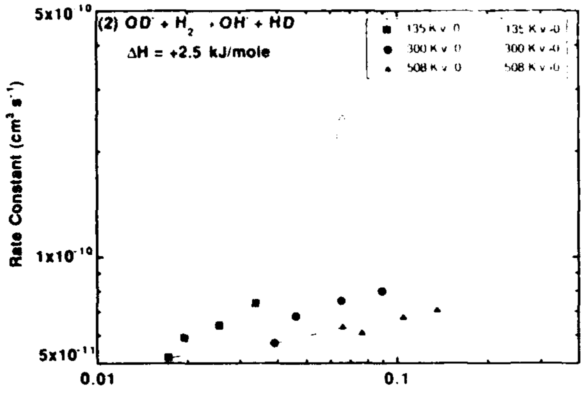

FIG. 3. Rate constants for the isotope exchange reaction of OD$^-$ with H_2 as a function of average kinetic energy, $\langle KE_{c.m.} \rangle$, at several temperatures. Data obtained with no added drift field are connected by a solid line (pure temperature dependence). Solid symbols refer to ground-state OD$^-$, and open symbols of the same shape refer to vibrationally excited OD$^-$ at the same temperature.

for the OD$^-$ reaction than for OH$^-$. It also may be harder to excite OH$^-$ due to its larger vibrational frequency.

Two previous studies of these reactions have been made. Grabowski *et al.*[16] measured the rate constants, at 300 K only, in an apparatus very similar to that used in the present experiments. In Table I, these values are compared with the present rate constants measured at 300 K. Grabowski *et al.* found rate constants 40% lower than the present values, essentially at the combined error overlap. The ratio of the rate constants, however, is in good agreement, within 10%. Meot-ner *et al.*[17] made temperature dependence measurements for reaction (1) in a high pressure mass spectrometer (HPMS). Their rate constant values are also lower than ours, while the temperature dependence measured in their experiment, although over the range 447–632, is similar to ours. The HPMS experiment was considerably more complicated than the selected ion flow tube experiments. In the HPMS, several gases were present at all times, and the rate constants could only be derived by modeling the data. It is unclear why the present rate constant values are higher than the previous ones. We measure all parameters used to derive a rate constant for each data point, and our data usually agree very well with literature values.[3,4,15,18] These measured parameters include the end correction and flight time as well as the more usual parameters such as ion signals, pressure, and temperature. Thus, we feel confident in our data but cannot rule out some unknown systematic error. If an error were to exist, it would likely be an absolute error, and our relative error limits would remain small. This is corroborated by the good agreement in the ratio of the rate constants of reactions (1) and (2) with those of Grabowski *et al.*[16]

TABLE I. Comparison of rate constants, in units of $cm^3 s^{-1}$, for the reactions of OH$^-$ with D_2 and OD$^-$ with H_2 measured at 300 K in the present study and by Grabowski *et al.* (Ref. 16).

OH$^-$+D_2		OD$^-$+H_2	
Present result	Grabowski *et al.*	Present result	Grabowski *et al.*
11.2×10^{-11}	6.8×10^{-11}	5.7×10^{-11}	3.8×10^{-11}

Three types of energy dependences can be obtained from the data. (1) The pure temperature dependence is given by the lowest energy point at each temperature, i.e., the point with no added drift field. In this case, $\langle KE_{c.m.} \rangle = (3/2)kT$. The pure temperature data are connected by a solid line to aid in viewing. (2) The kinetic energy dependence at each temperature is seen simply by following the symbol for that temperature. (3) Finally information on the internal energy dependence of the rate constant is obtained by comparing data taken at a fixed $\langle KE_{c.m.} \rangle$ but at different temperatures (interpolation is usually needed). For the present systems the internal energy dependence is due only to rotations since the vibrational frequencies of all the reactants are quite large. The rotational distributions are those of normal hydrogen, i.e., a statistical mixture of the *ortho* and *para* forms. For reaction (1), the rotational temperature of OH$^-$ is equal to $\langle KE_{c.m.} \rangle$ since D_2 has the same mass as the He buffer. Therefore for reaction (1), the only difference between data obtained at the same $\langle KE_{c.m.} \rangle$ but different temperatures is in the rotational temperature of the D_2. However, for reaction (2), the rotational temperature of OD$^-$ is greater than $\langle KE_{c.m.} \rangle$ (or equal to $\langle KE_{c.m.} \rangle$ when no drift field is applied) since H_2 is lighter than the He buffer. In this case, as the temperature of the buffer is raised at a fixed $\langle KE_{c.m.} \rangle$, the rotational temperature of OD$^-$ increases.

The data corresponding to OH(D)$^-$ in the vibrational ground state are quite different for the two reactions. Increasing temperature causes the rate constants for reaction (1) to decrease and the rate constants for reaction (2) to increase. Similarly, increasing $\langle KE_{c.m.} \rangle$ causes the rate constant for reaction (1) to decrease initially and reaction (2) to increase over our complete range of data. The reason for this difference is that reaction (1) is slightly exothermic and reaction (2) slightly endothermic. Therefore, the increase in the rate constant for reaction (2) with increasing temperature or $\langle KE_{c.m.} \rangle$ is due to overcoming a thermodynamic barrier.

The activation energy derived from the pure temperature data for reaction (2) is 0.27 kJ/mol (an activation energy of 0.75 kJ/mol is found from a quasi-Arrhenius treatment of the kinetic energy dependence at 135 K). The activation energy for reaction (2) is significantly less than the endothermicity of 2.5 kJ/mol. The results for reaction (1) offer an explanation for this. The rate constant for the exothermic reaction (1) decreases substantially with increasing temperature. This weakens the increase in rate constant expected from overcoming the barrier.

The "intrinsic" activation energy in reaction (2) may be derived by adjusting for the decrease in the rate constants with increasing temperature found for reaction (1). After normalizing for this temperature dependence, we find an activation energy of 1.9 kJ/mol for reaction (2). This value is in good agreement with the endothermicity of 2.5 kJ/mol, lending good support to the idea that the difference in the reactivity is essentially due to only the endothermicity of reaction (2). The actual situation must be more complicated since the positions of the transition states will also be affected by the thermicity. The good agreement between the intrinsic activation energy and the endothermicity does, however, show that the effect of the differing energetics of the two reactions explains much of the observed difference in the kinetics.

The decrease in rate constant with increasing temperature observed for reaction (1) is typical of ion–molecule reactions.[19] Several ideas have been put forward to explain the decrease with increasing temperature in ion–molecule reactions,[20,21] and it is difficult to be certain of the exact cause of the decrease for this reaction. The data for reaction (1) show minima in the $\langle KE_{c.m.} \rangle$ curves at each temperature. The minima are found at approximately 0.1 eV but seem to appear at higher energies with increasing temperature. Minima in the kinetic energy dependences are also typical of exothermic ion–molecule reactions. Frequently, the minima occur at energies near the cluster bond strength of the two reactants. The cluster bond strength of the two reactants[22] in this study is about 0.2 eV, in reasonable agreement with the energies at which the minima are found.

Perhaps the most novel result is the observation of a strong rotational temperature dependence. In reaction (1), any dependence on temperature at a particular $\langle KE_{c.m.} \rangle$ is due only to the different rotational temperatures of the D_2 neutral, since the average rotational temperature of the OH^- ion is equal to $\langle KE_{c.m.} \rangle$ and therefore fixed. The data in Fig. 1 show that at a $\langle KE_{c.m.} \rangle$ of 0.064 eV, the rate constant at 129 K is about a factor of 2.2 times higher than the rate constant at 507 K. This is a very large rotational temperature dependence. The 300 K rate constant has an intermediate value. A strong rotational dependence is seen for all temperatures and $\langle KE_{c.m.} \rangle$'s for this reaction. The rotational dependence is well outside the relative error of 15%.

The data for reaction (2) are slightly more complicated to interpret. At a fixed $\langle KE_{c.m.} \rangle$, not only does the H_2 neutral rotational temperature change but also the OD^- ion rotational temperature, since H_2 and He are not of equal mass. As explained above, at a fixed $\langle KE_{c.m.} \rangle$, the OD^- ion will have increasing rotational temperatures as the temperature of the buffer is raised. Therefore, both reactants have a higher rotational temperature as the temperature increases at a fixed $\langle KE_{c.m.} \rangle$. In addition, there is less overlap in the energy range between data at different temperatures, i.e., for only a few conditions are there data at more than one temperature at a fixed $\langle KE_{c.m.} \rangle$, and there are no conditions where data at a fixed $\langle KE_{c.m.} \rangle$ can be compared over the entire temperature range. This is due to the small mass of H_2 which requires that for a given laboratory ion energy or drift velocity, $\langle KE_{c.m.} \rangle$ will be less than for the D_2 neutral. Nevertheless, it is clear that the rotational temperature dependence is weaker for reaction (2) than reaction (1).

The smaller rotational dependence for reaction (2) could be due to a cancellation of rotational dependences in the two reactants, i.e., rotational excitation of H_2 decreases the reactivity as in reaction (1) and rotation of OD^- increases the reactivity. We believe a more likely explanation is that the rotational temperature dependence of reaction (2) is influenced by two factors, one positive and one negative. We speculate that the negative dependence is approximately the same as found in reaction (1) for the same unknown reason. The positive dependence is simply an activation energy effect, i.e., rotational energy is used to overcome the endothermicity of the reaction. We have observed one other instance where rotational energy clearly is employed in overcoming a reaction endothermicity, namely in the charge transfer reaction of Ar^+ with N_2.[6,23] These positive and negative influences offset each other but do not cancel, resulting in a smaller dependence than that found in reaction (1). We estimate, based on extrapolation, that at a fixed $\langle KE_{c.m.} \rangle$ of 0.064 eV, the rate constant at 135 K is about a factor of 1.5 times higher than the rate constant at 508 K, compared with the factor of 2.2 for reaction (1), in spite of the fact that rotational excitation in reaction (2) is present in both reactants. This interpretation is supported by the fact that the intrinsic activation energy matches the endothermicity.

The reason for the large rotational temperature dependence is unclear. In previous work, we have found that the rotational temperature of the neutral reactant usually has little effect on rate constants, i.e., differences in rate constants due to varying rotational temperature of the neutral are usually less than or equal to our relative error of 15%.[1–4,15,18,24–26] However, we have observed two notable exceptions. In the reaction of Ar^+ with N_2 we observed a large positive rotational dependence,[6] where N_2 rotational energy is used to overcome reaction endothermicity; this type of effect probably explains the smaller rotational dependence for reaction (2) relative to reaction (1). In the charge transfer reaction of Kr^+ with HCl, we found a large negative rotational dependence,[5] similar to that observed here. In the $Kr^+ + HCl$ reaction, it is believed that the rotational dependence is due to less effective locking of the HCl dipole to the Kr^+ charge as the HCl rotational temperature increases. Reaction (1) does not easily fit into either class of reaction that has previously been found to have a strong rotational dependence in the rate constant.

The room temperature data for reactions (1) and (2) have been explained by a triple well potential.[16] The entrance and exit channels are the $OH^- \cdot H_2$ isotopomeric complexes and the central complex is the more stable $H^- \cdot H_2O$ complex. This minimum energy pathway has been confirmed theoretically, and the energies of the minima and transition state have been calculated, although the calculations are known to be inaccurate.[27,28] Figure 4 schematically shows the approximate energetics of reaction (1). The energies given are not well-known, and the figure is meant to be a qualitative picture of the reaction potential energy. The well depths of the entrance and exit channels are quite small; it is not known whether there is a significant variation with angle. If there is, the rotational effect we observe here could then be due to a decrease in the rate of initial complex formation as the D_2 rotates faster, since

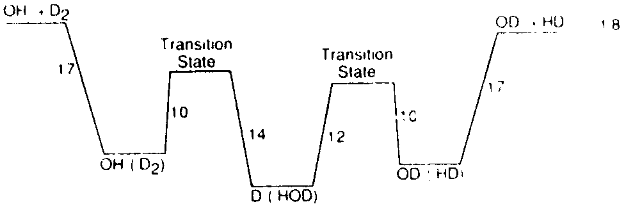

FIG. 4. Schematic of the potential energy diagram. Values refer to approximate energies relative to that of $OH^- + D_2$ in kJ/mol and are taken from Chalasinski *et al.* (Ref. 27). These values are not known with high certainty and are somewhat different than those found in Ortiz (Ref. 28).

it would be harder for the reactant to enter into the optimum geometry.

Another aspect of the present system is that the rotational constants of the neutral reactants are much larger than for any other molecule. This may make quantum effects more important. For other systems, rotations probably can be considered to behave classically at the temperatures of our experiments.

As part of a study of the chemistry of H_3O^-, we have found that OH^- clusters to H_2 slowly (i.e., inefficiently) at low temperatures.[22] At 90 K the association rate constant was found to be 1×10^{-30} $cm^6\,s^{-1}$ in a helium buffer. At the pressures of our experiments, the effective bimolecular rate constant is approximately 3×10^{-14} $cm^3\,s^{-1}$, over three orders of magnitude lower than the rate constants found for isotope exchange. The association rate constant will be even lower at the temperatures of the present experiments.[29] Therefore, the possibility that collisions between the buffer and the collision complex are responsible for the effect attributed to a rotational dependence can in all likelihood be excluded.

Modeling of the details of the reactions would be quite involved. As pointed out in Grabowski *et al.*[16] the reaction path involves three potential energy wells and two transition states. The details of the potential energy surface are not well-known.[27,28] Detailed modeling of these systems is well beyond the scope of this paper.

The above has pertained only to ground vibrational state reactants. Vibrational excitation of the reactant ion is found to increase the rate constant by a moderate to large amount. The vibrational level distribution of the ions was not determined in the present experiments. However, a large amount of vibrational excitation is observed ($\sim 30\%$), and therefore one would expect a large fraction of the excitation to be in the $v=1$ level with minor contributions from higher levels. The data for vibrationally excited reactant ions are shown in Figs. 1 and 2 as open symbols. For reaction (1), we could observe effects due to OH^- vibrational excitation for only a limited range of conditions. At low temperature, there was no evidence for the presence of vibrationally excited OH^-. For these conditions, the ground-state rate constant is substantially larger compared with higher temperature conditions. These last two facts probably indicate that, at low temperature, the excited and ground states react at similar rates, and therefore it would be difficult to observe a bimodal decay if vibrationally excited OH^- were present. Alternatively, helium may quench $OH^-(v>0)$ more effectively at lower temperature. This appears unlikely since vibrationally excited OD^- was observable at low temperatures.

The data indicate that there may be temperature, kinetic energy, and rotational energy effects in the rate constants for the vibrationally excited ion species. Although one might expect dependences on these various types of energy, our error limits are quite large for the $v>0$ data, and it is not possible to be certain whether these effects are real. Therefore, with regard to the vibrationally excited ions, at present it is only possible to be confident that vibrational energy increases the reactivity. To the best of our knowledge, the present systems, along with our recent results on the reaction of O_2^- with SF_6, are the first measurements of rate constants for vibrationally excited negative ions.

In summary, we report a wealth of data on isotope exchange reactions between OH^- and H_2 for two of the four isotopic variants. Reaction rate data are presented as a function of temperature and kinetic, rotational, and vibrational energy. Reaction exothermicity plays a significant role in the reactions. All types of energy seem to be able to drive the reaction when endothermic. The least understood aspect of the data is that rotational excitation decreases the reactivity. The rotational temperature effect was unexpected and is at present unexplained, warranting theoretical calculations.

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