Deuterium Effect on the Pressure Coefficient of the Tunneling Rate in the Acridine−Fluorene Solid-State Photoreactive System

I. Y. Chan* and A. J. Hallock[†]

Department of Chemistry, Brandeis University, P.O. Box 9110, Waltham, Massachusetts 02454-9110

B. Prass and D. Stehlik

Fachbereich Physik, Free University Berlin, Arnimallee 14, D-14195 Berlin, Germany

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We report the pressure effect on the intermolecular deuterium transfer tunneling rate in the acridine-doped fluorene crystal at 77, 150, and 200 K. Similar to the hydrogen transfer, the tunneling rate is exponentially enhanced by pressure. The pressure slope for this exponential enhancement, however, is found to be more temperature dependent for deuterium than for hydrogen tunneling. The ratio of the pressure coefficients for H and D stands at 2.6 at 77 K, gradually decreasing with increasing temperature until it becomes essentially unity at room temperature. An intuitive model based on the mass dependence of the tunneling distance is presented to rationalize these observations.

I. Introduction

Upon photoexcitation of an acridine/fluorene (Ac/Fl) mixed crystal, the aza center of the Ac in the excited triplet state abstracts a hydrogen atom from the methylene group of a specific Fl neighbor via a quantum tunneling mechanism. It is one of the most experimentally accessible vehicles for studying hydrogen tunneling in a fixed reaction geometry. Consequently, in recent years, this Ac/Fl photosystem has increasingly become the focus of theoretical analysis as well. In a series of publications, Prass, Stehlik, and co-workers investigated in detail the temperature dependence of its tunneling rate and identified a long axis libration as a major promoting mode.[1−3] Further insight was obtained in recent years by employing pressure as an additional experimental parameter.[4−6] For a short review of the distributed data on the Ac/Fl system see ref 7. Generally speaking, the pressure dependence of the decay rate of the Ac triplet precursor state may be described as the sum of a nearly pressure-independent intramolecular triplet decay rate of the Ac and a hydrogen transfer tunneling rate with a characteristic exponential growth under increasing pressure. Under this framework, we were able to extract the tunneling rate from the vibrational ground state at the limit of low temperature, which up to that time could not be meaningfully measured due to the obscuring effect of the intramolecular decay.[5] With Raman spectroscopy under pressure, we identified an additional butterfly mode of Fl as a suitable promoting mode, and demonstrated through simulation a synergistic effect of multiple promoting modes in enhancing tunneling.[6] Pursuant to the availability of empirical data, theoretical calculations have proceeded in stride.[8−11] Among these works, we wish to mention a recent paper by Trakhtenberg and Klochikhin which modeled both the temperature and more recent pressure dependence of the tunneling rate of the Ac/Fl system.[11] These authors were able to fit all available pressure-dependence data covering four temperatures from 1.4 to 300 K with only one adjustable parameter.[11] Such an attempt in synthesis, although it may not yet be definitive, is certainly a major step in the right direction.

From a phenomenological point of view, there are several hallmarks for a tunneling reaction: (1) a non-Arrhenius temperature dependence and the associated asymptotic low-temperature residual reaction rate, (2) a large kinetic H/D isotope effect, and (3) a hypersensitive, (nearly) exponential growth of tunneling rate under increasing pressure. Among these, (1) and (3) have been extensively documented by experimental works spanning over more than a decade, principally focused on, but not limited to, the Ac/Fl system.[1−6] The kinetic isotope effect, in comparison, has not been fully investigated. This paucity of works in the literature does not reflect the lack of significance of the phenomenon. Rather this is a result of its experimental difficulty. Quite often, the effect on tunneling upon deuteration, for example, is so great that the tunneling of a deuterium may easily be obscured by competing processes. For example, Prass et al. were able to extract the deuterium tunneling rate only over a limited temperature range between 300 and 200 K.[2] A notable exception is the keto−enol tautomerization of 2-(2′-hydroxypheny)benzoxazole (HBO) and its *m*-methyl-substituted analogue (*m*-MHBO) investigated by Grellmann and co-workers.[12,13] These systems have characteristic rates in the microsecond range for the H species and in the millisecond range for the D species. Grellmann et al. therefore were able to measure the effect of deuteration on tunneling over a wide temperature range. The isotope effect for HBOs increases from about 20 at 220 K to over 10^3 at 45 K in an asymptotic manner. Since the HBO system enjoys the unique position of being the only one with comprehensive data of the deuterium effect on tunneling, it is tempting to take it as a prototype in consideration of other systems. However, we should keep in mind that our ability to generalize may be limited by dissimilarity in chemical nature of the photoreactions in the different systems.

In this paper, we report an investigation of the deuterium isotope effect using pressure as a variable. The central idea is that pressure, enhancing the tunneling rate exponentially, may

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* Author to whom correspondence should be addressed.

[†] Present address: Department of Chemistry, Stanford University, Stanford, CA.

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render the tunneling of deuterium observable in a wider range of temperatures. In this methodology, the pressure coefficient of the exponential enhancement is measured for Fl with deuterated methylene at various temperatures. These coefficients are then compared with the corresponding values for the normal hydrogen abstraction. This effort achieved only partial success, for we were hampered by the effects of a phase transition which occurred at an intermediate pressure range (30−40 kbar). The high-pressure phase apparently has a crystalline packing more favorable to the hydrogen abstraction reaction, for in this phase, the phosphorescence of Ac was totally quenched. As a result of this limitation, we completed the measurement at 77 K with some difficulty, whereas we judged that experiments at liquid helium temperature are not feasible. Thus we were deprived of the most important comparative study between the two isotopic species, the tunneling rate from the vibrational ground state. In this article, we report our results for the deuterium abstraction at 77, 150, and 200 K. The results at 300 K have previously been published.[4] Coupled with the data for the H species,[4−6] these new data constitute a first investigation of the deuterium isotope effect for the Ac/Fl system using pressure as a tool.

II. Experimental Section

The 1000 ppm perdeuterated Ac/Fl crystal was grown by the Bridgeman method. The pressure generation and calibration techniques as well as phosphorescence lifetime measurement apparatus have been described in detail.[4−6] For the 77 K experiments, we used an immersion-type cryostat and nitrogen laser (337 nm) excitation. For 150 and 200 K, we used an APD Displex DE204SL closed cycle refrigerator controlled by a Lakeshore 320 temperature controller. The APD device has a sample-in-vacuum design, we therefore had a legitimate concern of thermoconductivity. The diamond anvil cell (DAC) was constructed with Be−Cu for better low-temperature heat conduction. A Lakeshore DT470 diode thermometer was mounted at the upstream (along the heat path) flange of the DAC. To avoid oscillation problems, we control temperature at the tip of the refrigerator. The two diode thermometers showed readings within the specified accuracy of the two devices. Usually the diode at the DAC shows slightly lower temperature for our experiment. Presumably there was some radiative cooling, for the radiation shield was at about 40 K. The 150 and 200 K experiment used the 355 nm light from a tripled Nd:YAG laser for excitation.

As mentioned in the Introduction, there is a phase transition leading to total quenching of Ac phosphorescence. The critical pressure for the phase transition is not known and difficult to assess, for the transition is extremely sluggish, sometimes taking hours at room temperature to complete the process. It suffices to say that at 77 K, we have actuated the phase transition when the system pressure was above 30 kbar. Indeed, we have taken advantage of this metastability to conduct our 77 K experiments. Namely, data were taken at pressures much higher than 30 kbar before the phase transition was complete. Our apparatus was not designed to change pressure while the DAC was in a cryostat. A special operational procedure was devised to accomplish cold compression. In this scheme, the DAC was adjusted to 25−30 kbar as a jump-off point for cold compression. The experimental apparatus was then taken out of the cryostat into a nitrogen-flushed glovebag while the DAC was immersed in liquid nitrogen. The DAC was taken out of liquid nitrogen momentarily for raising pressure while cold, then transferred back to the cryostat again for measurement. To avoid temperature change, the compression was conducted “blindly”, i.e., without the monitoring benefit of a micrometer. Trial and error got the system to a pressure of interest from the jump-off point. This scheme subjected the diamond anvils to considerable risk, although it did accomplish the mission. We did not attempt to perform experiments at liquid helium temperature, for we anticipated its need to go to a much higher pressure. The aforementioned procedure therefore presented unacceptable risk.

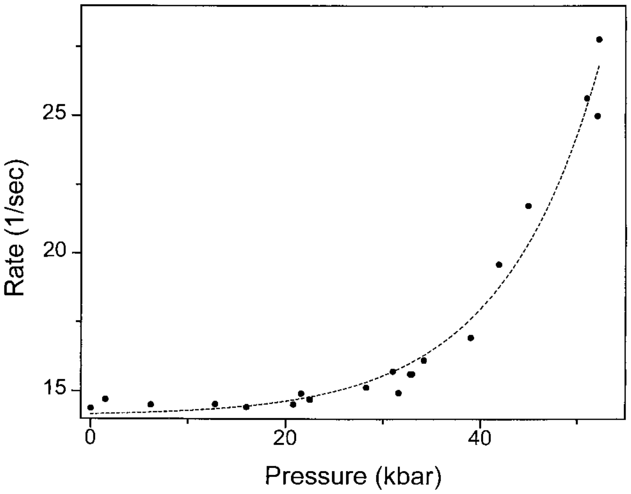

Figure 1. The apparent triplet decay rate at 77 K as a function of pressure. Perdeuterated Ac/Fl. This figure shows the worst-case quality of our data, see text. The line of short dashes is the best fit of eq 1 to the data.

III. Results

We have measured the pressure dependence of the D transfer tunneling rate for perdeuterated Ac in perdeuterated Fl at 77, 150, and 200 K, in addition to earlier room-temperature data.[4] As mentioned above, the higher pressure part of the experiment at 77 K was conducted through cold compression. We found that an abrupt increase of pressure tended to trigger the phase transition, thereby defeating the purpose of the operation. If the cold compression was made gentle enough, we observed some phosphorescence, as judged by its spectrum, with a lifetime in the expected range. The intensity of the phosphorescence, however, was typically only about 10% of what might be expected. Although metastability of the low-pressure phase made the experiment possible, it seemed that the crystal was not homogeneous. Instead, domains existed in the crystal corresponding to the existence of both the high- and low-pressure phases. Only domains in the low-pressure phase contributed to the observed signal. Partly because of this inhomogeneity, partly because the cold compression process introduced some pressure gradient, the data quality at 77 K was poorer than that from normal operation. This is apparent from Figure 1. Data for 150 and 200 K were of higher quality. For the 150 K experiment, we encountered the same phase transition problem above 26 kbar. Our cold compression technique is not applicable to the closed-cycle refrigerator system. Thus the 150 K data has a shorter dynamic range. The full three sets of data are plotted in semilog format in Figure 2. It is not surprising that an exponential rise above the intrinsic triplet decay of Ac, as observed before for the protonated Fl,[4−6] is valid for the deuterated species also. More important in the present context, this figure emphasizes the fact that the pressure slope for the tunneling rate is increasing significantly with increasing temperature.

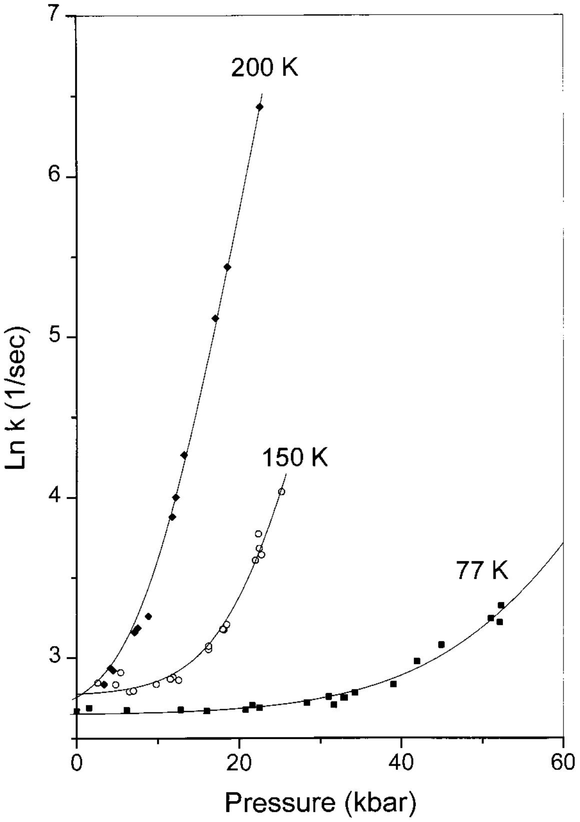

Figure 2. The complete set of apparent triplet decay rate as a function of pressure in semilog format for the three temperatures 77, 150, and 200 K. Perdeuterated Ac/Fl. This figure clearly demonstrates the strong increase of the pressure slope with increasing temperature. The solid lines are the respective best fits of eq 1 to the data. The resultant parameters are listed in Table 1.

The raw data k_{T1A}, the apparent phosphorescence decay rate of the Ac triplet, were fitted to the sum of a constant plus an exponential rise according to eq 5 of ref 5:

$$k_{T1A}(T,P) = k^{i}(T) + k_{TR}(P = 0)\exp[S(T)P] \qquad (1)$$

Here k^i is the intramolecular decay rate, established to be nearly pressure independent, $k_{TR}(P = 0)$ has the significance of a tunneling rate as extrapolated down to ambient pressure from our high-pressure data, and S is the pressure coefficient of the tunneling rate. It was through this extrapolation procedure that we determined the low-temperature tunneling rate from the vibrational ground state in ref 5. The dashed line in Figure 1 is the computed function from the best fit of eq 1 to our data. In the present case, however, due to the long extrapolation from a clearly exponential high-pressure region to ambient pressure, our ability to extract a reliable value of $k_{TR}(P = 0)$ is limited. Our data, through this fitting procedure, have more significance in accurately determining the pressure slope S at 77 K. Similar reservations, to a lesser extent, also apply to the 150 and 200 K data.

The resultant parameters are listed in Table 1. For comparison, we have included the corresponding values for the undeuterated species. To make a quantitative comparison, data from previous publications[4−6] with different levels of accuracy have been refitted to obtain estimations of error. The value of these newly obtained parameters may be slightly different from those already published in the literature, although these minor revisions will not change the physical picture significantly. The number in the parentheses after each value of the parameters is the standard deviation *of the mean* as propagated through the rules of statistics. The only exception in this refitting operation is the data at 300 K. These early data, especially those for the H isotope, were of much cruder quality. It is our judgment that a more quantitative refitting is not warranted. Independent of this, it is clear from Figure 1 of ref 4 that the pressure slopes for the two isotopic species are identical within experimental accuracy. Thus, these early data help establish the trend in the ratio of S as a function of temperature.

IV. Discussion

One of the key features of our results is that the pressure coefficient S is a rather strong function of temperature in deuterium transfer. For tunneling of normal hydrogen, S is also increasing with temperature above 77 K, but far less. Quantitatively, the ratio S_H/S_D for the two isotopic species, is about 2.6 at 77 K, and diminishes with increasing temperature until it approaches unity at room temperature. In ref 6, we attributed the temperature dependence of S to a thermally induced change in compressibility. We believe that this picture is still correct. However, a contribution to the temperature dependence by a compressibility change is expected to be the same for both isotopes, for the two samples differ only in the two bridge methylene hydrogens. The decreasing ratio of the pressure coefficients between the two isotopic species as temperature increases toward ambient value, however, is a new observation which must have its origin in the mass dependence of the tunneling process. This is a new aspect of the isotope effect on tunneling. Together with the temperature effects, it may shed new light on the tunneling process.

On a rudimentary level, our observation is not difficult to comprehend. For discussion's sake, let us employ the harmonic potential. Consider first tunneling from the zero-point vibrational state. For a given tunneling geometry, the effective tunneling distance has to take into account the root-mean-square displacement of the tunneling particle from the configuration of minimum potential energy. This quantity is mass dependent, being smaller for deuterium than for hydrogen (see below).

TABLE 1: Summary of High-Pressure Kinetic Data at Various Temperatures

temperature (K)	isotope	S (e/kbar)	$k_{TR}(P = 0)$ (s^{-1})	S_H/S_D	ref
1.4	H	0.2403(0.0014)	1.45(0.06)		5
77	H	0.2480(0.0043)	2.95(0.25)	2.57(0.08)	4
77	D	0.0967(0.0025)	0.082(0.011)	2.57(0.08)	this work
150	H	0.3635(0.0045)	15.74(0.79)	1.68(0.04)	6
150	D	0.2161(0.0042)	0.181(0.018)	1.68(0.04)	this work
200	D	0.2597(0.0010)	1.731(0.037)		this work
300	H	0.372(−)		1.0(−)	4
300	D	0.372(−)		1.0(−)	4[a]

[a] We found a numerical error in ref 6 on p 2963 following its eq 1. In that attempt to refit the deuterium tunneling rate at 300 K, we used a database in which the kinetic rates were mistakenly too large by a factor of 10. The results of that fitting, therefore, are not valid and should be ignored.

Mathematically, the wave function is a Gaussian function whose width is smaller for deuterium than for hydrogen. It implies that a deuterium particle is less probable to be found in the classically forbidden region than a hydrogen. In a Golden Rule Approach[14] in computing tunneling rate, this fact results in a smaller Franck−Condon factor. In any other static or dynamic double minimum potential picture, the effective tunneling distance is larger for D than for H. Thus we expect a H/D isotope effect at low temperature. With increased pressure, mainly the intermolecular distance is reduced and this is essentially the same for H and D tunneling. However, the tunneling distance is greater for D than for H tunneling, hence the percentage of distance change is smaller for D than for H tunneling. By this reasoning, we may expect a lower pressure coefficient for deuterium tunneling than that for hydrogen tunneling from the zero-point level.

Next we must explain the fact that the ratio of the pressure coefficient for the two isotopes approaches unity at higher temperature. In a harmonic oscillator wave function implicit in mass,

$$\psi_n = N_n H_n(y) \exp[-y^2/2]$$

$$y \equiv (m\omega/\hbar)^{1/2}\, q,\ q \equiv x - x_0$$

H_n is the Hermite polynomial of degree n, and the other symbols have the usual meaning. It is a textbook exercise to show that $\langle y^2\rangle = n + {}^1/_2$. For a given n, such as $n = 0$, $\langle y^2\rangle$ is a constant. Thus

$$\langle q^2\rangle = [\hbar/(mk)^{1/2}]\, \langle y^2\rangle$$

The mean square displacement is inversely proportional to $m^{1/2}$. (This corroborates the statement in the last paragraph.) At higher temperature, we may speak of an average level of thermal excitation of vibrational motion by introducing a quantity $\langle n\rangle = \langle E_\mathrm{v}\rangle/\hbar\omega$ which is higher for deuterium than for hydrogen due to a lower vibrational frequency.

$$\langle q^2\rangle = [\hbar/(mk)^{1/2}]\, (\langle n\rangle + {}^1/_2)$$

Therefore the two sources of mass dependence will partially cancel. In the limit of high temperature, $\langle E_\mathrm{v}\rangle = kT$, $\langle n\rangle$ is proportional to $m^{1/2}$, and the cancellation will be exact. The difference between the pressure coefficient S at lower temperature for the two isotopes will diminish at higher temperature. With this qualitative argument, we may therefore rationalize our observation that the S value for the two isotopes becomes less different at higher temperature. It would nevertheless be desirable to demonstrate that this postulated effect is of the right order of magnitude compared to that of the observation.

In the Appendix, within the framework of the Golden Rule Approach,[14] we develop an expression for the pressure dependence of the Franck−Condon factor (FCF) in close form which shows a mass dependence for tunneling between two zero-point levels, see eq 4 of Appendix. In essence, the change of the FCF with tunneling distance R is proportional to the FCF itself. Further, as shown at the end of the Appendix, the tunneling rate scales with mass ratio $m' \equiv (m/m_\mathrm{H})$ as $m' \exp(-4\sqrt{m'})$. For deuterium vs hydrogen tunneling, this suggests an isotope effect of $(1/2)e^{5.6}$ on S at low temperature. This figure grossly overestimates the deuterium effect, and there is an obvious reason. The Ac/Fl tunneling has a large exothermicity, and the receiving state has vibrational energy of about 2 eV. As reasoned above, under such conditions (of large n), there is no isotope effect on the receiving side. Thus a more reasonable estimate of the deuterium isotope effect from the zero-point state of the fluorene is $(1/2)e^{2.8} = 8.2$, assuming a mass ratio of 2. For reasons deliberated in the next paragraph, this magnitude should be considered an upper limit. Compared with the observed ratio of 2.6-fold at 77 K, our simple model has succeeded in providing an order-of-magnitude account of the phenomenon.

Indeed, a mass ratio of 2 upon deuteration may not at all be appropriate. In our experiment, deuteration operationally means a deuterium substitution of the two hydrogens at the methylene bridge of Fl. Under a normal mode scheme, due to the combined motion of many masses, this isotopic substitution results in a ratio of reduced mass much less than a factor of 2. This is also true for the butterfly mode of Fl,[6] although less severe than for the promoting librational phonon mode. Along this line of reasoning, it may be necessary to revise our estimate above further downward, perhaps even toward the low side of the same order of magnitude with the observed ratio. In this context, we note that, a recent publication of Trakhtenberg and Klochikhin[11] adopted a “one frequency approximation”. Instead of considering three or four promoting modes each with a frequency around 100 cm^{-1}, they found it sufficient to describe published experimental data[1−6] by invoking only one effective frequency Ω_0. Besides obvious advantages in simplifying computation, this approach has a further conceptual appeal. Insofar as the promoting modes are all phonons, Ω_0 has the significance of the Einstein frequency. One may choose an advantageous linear combination of these phonon modes to represent the effect of lattice vibration on tunneling. Carrying this idea one step further to include the molecular modes of Fl, such as the butterfly mode(s), such a linear combination of normal modes approaches the local mode picture of Henry,[15] in which the tunneling particle undergoes effective vibrational motion along approximately the reaction coordinate. The physical insight provided for each of the individual promoting modes is lost here. In return, one gains the conceptual simplicity of a one-dimensional vibrational promotion of tunneling of the H or D particle. From the latter perspective, the mass ratio upon deuteration will again approach 2, as we have used in the last paragraph. The merit of each of these two alternative ways to look at a tunneling reaction certainly warrants further consideration.

An interesting aspect of this work lies in the identification of two different contributions to the pressure coefficient $S(P)$ of a tunneling system. We have mentioned in ref 6 that a temperature-dependent compressibility may be the origin of the temperature dependence of $S(P)$ in the tunneling process. Isothermal compressibility (k_T) is independent of temperature near 0 K, and is monotonically increasing at higher temperature. Qualitatively, this temperature dependence, $k_T(T)$, is consistent with the earlier observed temperature variation of $S(P)$. On the other hand, the very small molecular perturbation by deuteration of the methylene bridge of Fl is not expected to change the compressibility of the fluorene crystal. Nevertheless, we observe a major difference in the pressure coefficient $S(P)$ with the change of the tunneling particle from H to D, which cannot be attributed to $k_T(T)$. At present, our data are too sketchy to warrant a clear-cut separation of the two contributions to $S(P)$. However, with a more comprehensive understanding of the isotope effect on tunneling it may even be possible to obtain reliable information on the $k_T(T)$ dependence from a sufficiently accurate data set for $S(P,T)$.

As mentioned in the Introduction, the HBO is the only system which has both H and D tunneling data available over a wide temperature range, including the low-temperature limit. The feature of the HBO results[12] is that the deuteration effect increases at lower temperature to over a factor of 10^3. It is tempting to interpret this as a prototypal behavior. However, we should not lose sight of the difference in the nature of the tunneling process in the HBO and the Ac/Fl systems. The former system has a tunneling distance considerably shorter than that for the latter. Further, HBO has a barrier of only about 40 kJ[12,16] (3.4×10^3 cm^{-1}) compared with about 10^4 cm^{-1} for Ac/Fl. This difference in parameters is reflected in the factor of 6 orders of magnitude in the absolute tunneling rates between these two systems. With such contrast in physical characteristics between the Ac/Fl and HBO systems, a pressure coefficient measurement of the latter will be an interesting comparative study. Such measurements for the *m*-methyl HBO are currently in progress. Lastly, Trakhtenberg and Klochikhin[11] estimated the low-temperature deuterium effect in Ac/Fl to be e^{10} which is some 13-fold higher than that for the HBO system. Further, it has not taken into account our new-found isotope effect on the pressure slope $S(P)$. Although computationally the lower $S(P)$ for D tunneling is ill-suited for an accurate extraction of $k_{TR}(P = 0)$, our model on the basis of longer tunneling distance for deuterium (due to a smaller $\langle q^2 \rangle$) suggests a lower $k_{TR}(P = 0)$ for D tunneling over and above the expected isotope effect in any static tunneling model. It will further accentuate the isotopic ratio of $k_{TR}(P = 0)$ in favor of H tunneling. It appears that a theoretical estimate of the kinetic isotope effect in tunneling reactions needs further improvement.

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Appendix

We wish to evaluate the pressure dependence of the Franck–Condon factor for tunneling between two zero-point states displaced by a distance R. The overlap integral of the two vibrational wave functions may be written as

$$I = (m\omega/\hbar\pi)^{1/2} \int_{-\infty}^{\infty} \exp\{-(m\omega/2\hbar)[q^2 + (q - R)^2]\}\, dq \quad (1)$$

We are interested in $(\partial I/\partial R)$ under pressure,

$$(\partial I/\partial R) = (m\omega/\hbar)\{(m\omega/\hbar\pi)^{1/2} \int q\, dq \times \exp\{-(m\omega/2\hbar)[q^2 + (q - R)^2]\} - RI\} \quad (2)$$

The integral in the first term in the curly bracket has contribution from q only around $q = {}^1/_2R$. Thus the first term is approximately equal to ${}^1/_2RI$

$$(\partial I/\partial R) \approx (m\omega/\hbar)\,(-{}^1/_2RI) \quad (3)$$

The negative sign is consistent with the physical intuition that, under pressure, R decreases and the rate will increase. Thus the overall R-dependence of the Franck–Condon factor is

$$(\partial I^2/\partial R) = 2I(\partial I/\partial R) = -(mk)^{1/2}\,(R/\hbar)\,I^2 \quad (4)$$

For further discussion of deuterium isotope effects, it is convenient to introduce a mass ratio m', the ratio of the mass of the particle of our concern to the mass of hydrogen. m' may be construed as a "dimensionless mass", a parameter which we change in our isotopic studies. Now, eq 1 contains an overlap integral whose two functions each scale with $\exp(-\sqrt{m'})$. Therefore I^2 scales with $\sqrt{m'}\ \exp(-4\sqrt{m'})$. The distance dependence of the Franck–Condon factor scales with $m' \exp(-4\sqrt{m'})$. These results will be used in the Discussion section of the text.

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