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Bonding Theory

Fundamental Change in the Nature of Chemical Bonding by Isotopic Substitution**

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Abstract: *Isotope effects are important in the making and breaking of chemical bonds in chemical reactivity. Here we report on a new discovery, that isotopic substitution can fundamentally alter the nature of chemical bonding. This is established by systematic, rigorous quantum chemistry calculations of the isotopomers BrLBr, where L is an isotope of hydrogen. All the heavier isotopomers of BrHBr, BrDBr, BrTBr, and Br^{4}HBr, the latter indicating the muonic He atom, the heaviest isotope of H, can only be stabilized as van der Waals bound states. In contrast, the lightest isotopomer, BrMuBr, with Mu the muonium atom, alone exhibits vibrational bonding, in accord with its possible observation in a recent experiment on the Mu + Br$_2$ reaction. Accordingly, BrMuBr is stabilized at the saddle point of the potential energy surface due to a net decrease in vibrational zero point energy that overcompensates the increase in potential energy.*

Since the discovery of deuterium,[1] isotopic substitution and its effect on molecular properties and reaction dynamics has played an important role in chemistry.[2,3] However, deuterium is only twice as heavy as hydrogen, and though tritium is three times as heavy, it has seen only limited use since it is dangerously radioactive. Hence it has fallen to muon science[4–6] to broaden the H-atom isotopic mass scale, from muonium (Mu = μ^+e^-), with a mass of 0.114 u,[4,5] to muonic helium (^{4}H = [^{4}He$^{++}\mu^-$] + e$^-$), with a mass of 4.116 u.[7–9] Here we establish a new quantum isotope effect in which the substitution of Mu for H in the BrHBr radical can fundamentally change the nature of chemical bonding.

Conventionally, the formation of chemical bonds is due to a decrease in potential energy (PE), often accompanied by small increases in vibrational zero point energy (ZPE). In principle, this basic mechanism can be completely reversed, wherein chemical bonds may even be formed by an increase in PE if there is a sufficiently compensating decrease in vibrational ZPE, giving rise to what has been coined "vibrational bonding" of molecules stabilized at saddle-point barriers on a potential energy surface (PES), far away from potential minima. Though this purely quantum mechanical phenomenon is well known,[10–18] the stabilization of vibrationally bound states has heretofore not been convincingly demonstrated.[19] This communication presents the first clear evidence for their existence, established through high-level quantum calculations of the eigenstates of the products BrLBr formed by isotopic substitution in the Br + LBr reaction over the remarkable range of a factor of 36 in H-atom (L) isotopic mass, from ^{4}H, T, D, H, to Mu.

Both BrHBr and BrDBr have been detected by photodetachment electron spectroscopy of their anionic precursors;[20–22] they have also been isolated in Ne and para-H$_2$ matrices.[23,24] Recent experimental evidence suggests that the BrMuBr radical may be formed as a product of the Mu + Br$_2$ reaction,[25] in accord with earlier theory.[26] Van der Waals (vdW) bonded eigenstates of BrHBr with bent and slightly more stable linear (hydrogen-bonded) geometries have also been calculated on a PES that includes spin–orbit coupling (SOC), determined in the vicinity of these vdW potential minima (though not at the potential barrier).[27] The experimental photodetachment studies clearly demonstrate that the BrHBr and BrDBr radicals are not vibrationally bound.[20–22] An earlier claim[16] of vibrational bonding in BrHBr is thus incorrect, due to potential barriers assumed in the semiempirical PESs used then that were too low, compared to later quantum chemical calculations,[26] also shown herein.

The essence of the quantum mechanical mechanism of vibrational bonding was formulated in a series of papers on the IHI system,[10,12,14–18] also treated semiclassically.[11,13] Symmetric heavy–light–heavy XLX radicals, with an H atom isotope (L) between two heavy halogens (X), are expected to be ideal candidates for vibrational bonding, if the barrier on the PES is not too high. In contrast to conventional bonding, the effect of ZPE increases with the mass ratio m_X/m_L[16,17] in the case of vibrational bonding. Consequently,

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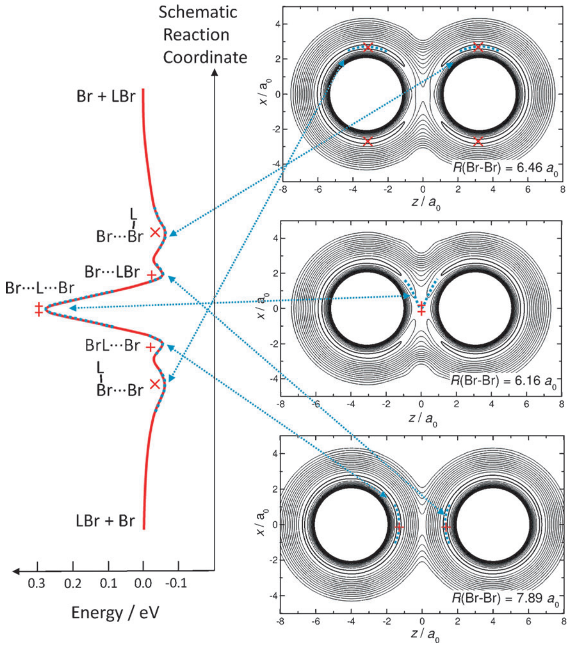

Figure 1. Potential energy surface (PES) of the isotopomers BrLBr with L = Mu, H, D, T, or ^{4}H. The three-dimensional (3D) global PES is exemplified by three 2D equipotential contour diagrams (ECDs) reminiscent of a "figure eight" (right). The corresponding distances R(Br–Br) between the Br nuclei are fixed at the values 6.16, 6.46, and 7.89 a_0 for the potential barrier (red ‡) and for two types of van der Waals minima (red × and +). The blue arrows indicate the construction of the potential energy profile along the schematic reaction coordinate.

Table 1: Comparisons of selected properties for the stationary points of the potential energy surface for BrHBr and its isotopomers.

Property	R_{HBr} [a_0]	R_{BrBr} [a_0]	θ [°][a]	Energy [eV][b]
Linear vdW minimum $C_{\infty v}$				
MRCI + Q/AVTZ[c]	2.69	7.98	180.0	−0.053
RCCDD(T)/AVQZ[d]	2.67	8.01	180.0	−0.055
Bent vdW minimum C_s				
MRCI + Q/AVTZ[c]	2.69	6.46	73.4	−0.059
RCCDD(T)/AVQZ[d]	2.67	6.92	78.7	−0.042
Transition state $D_{\infty h}$				
MRCI + Q/AVTZ[c]	3.08	6.16	180.0	0.286

[a] Br-H-Br angle. [b] Energy measured from the asymptotic Br + HBr potential minimum. [c] Present work. [d] From Ref. [27].

though not viable for BrHBr[20,22] and BrDBr[20] (or for BrTBr, Br^{4}HBr), vibrational bonding could be stabilizing in BrMuBr,[25,26] providing motivation for the present study. Establishing this, though, demands accurate calculations and interpretation of the eigenstates of BrLBr, an open-shell system. For this purpose we have calculated a new global three-dimensional (3D) (Born–Oppenheimer) PES at the MRCI + Q/AVTZ level of quantum chemistry, well beyond the semiempirical PESs used in the earlier studies[10–19,21] and also beyond that utilized in Ref. [26], though also without SOC.

This global surface is illustrated in Figure 1 by three characteristic equipotential contour diagrams (ECDs) and by a schematic 1D potential energy profile (the red curve). There are two different types of vdW minima corresponding to bent (red "×") and linear (red "+") structures, separated by the potential barrier at the transition state (TS, red "‡"), which has a linear BrLBr structure.

The properties of these stationary points are given in Table 1 (see also Figures 2, 3, and 4). Comparisons with the results for the vdW minima from the calculations of Toboła et al.,[27] restricted to regions of the surface in the domains of these minima, only, are also given. Though their geometries and energies are obtained at an even higher level of quantum chemistry than the present results, the level of agreement seen in Table 1 affirms the high quality of the present global PES, which is the most accurate yet reported in the barrier region.

The wavefunctions and energies of the ground states of all isotopomers of BrLBr are evaluated on this new global PES using the method of Ref. [28] (for details see the Computational Section). The resulting quantum mechanical probability densities (corresponding to the squares of the wavefunctions) and their total energies (PE plus ZPE) are illustrated in Figure 2 for the lightest isotopomer, BrMuBr, and in Figure 3 for the heavier ones, exemplified by BrDBr (a) and BrHBr (b). In these latter cases the 3D

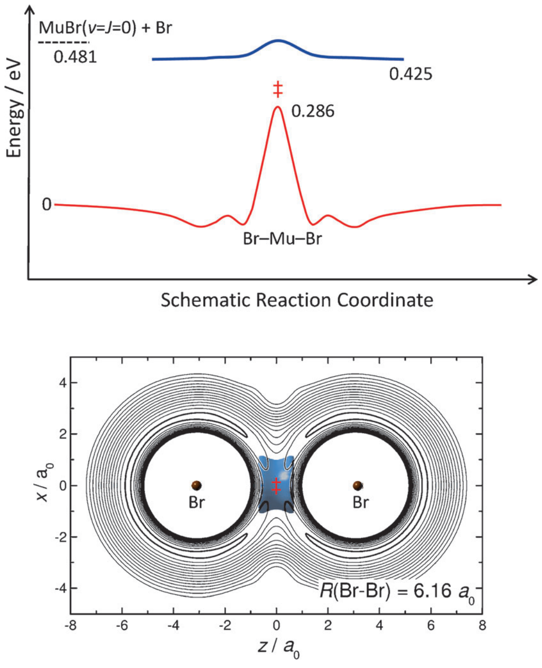

Figure 2. Vibrational bonding of the lightest isotopomer, BrMuBr. The bottom panel shows a 2D equipotential contour diagram (ECD) of the PES, with symbols as in Figure 1, together with the quantum mechanical structures of linear BrMuBr. The heavy Br nuclei are localized in the domains of the small brown spheres close to the twin centers of the "figure-eight" ECD. The 3D probability distribution of the central Mu atom is illustrated by purple equidensity contour (for the value that corresponds to 66% of the maximum density) and appears as a purple double cone centered at the potential barrier (red ‡). This is also illustrated by the purple line for the probability density shown above the schematic 1D energy profile, adapted from Figure 1.

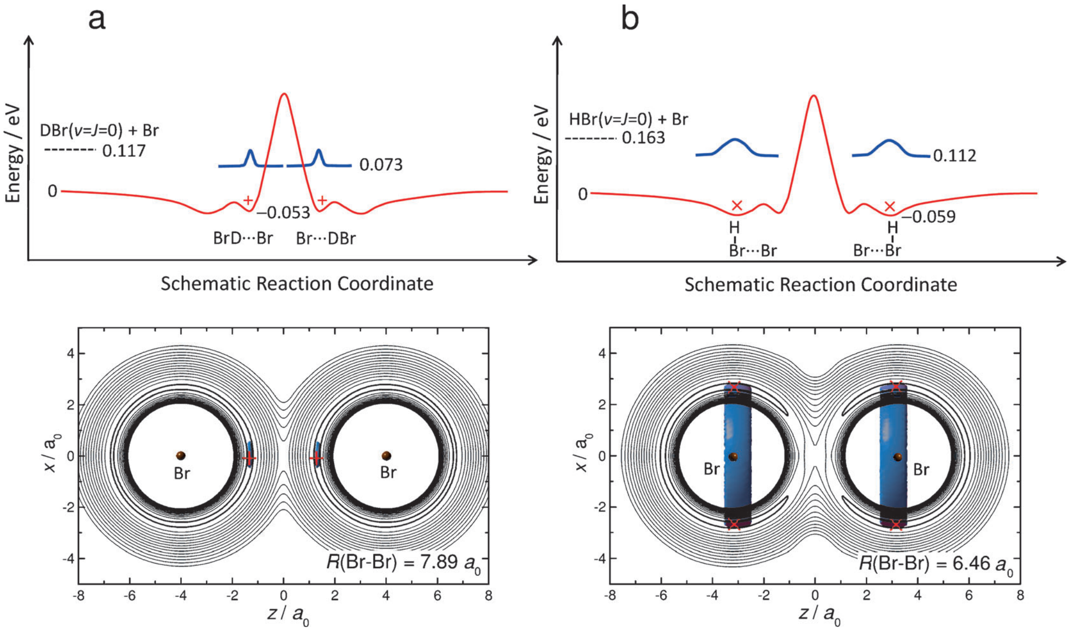

Figure 3. Van der Waals bonding with linear (a) and bent (b) structures of the heavy isotopomers BrLBr with L = H, D, T, ^{4}H. Notations analogous to those in Figures 1 and 2. The 3D quantum mechanical probability densities of the nuclei of the L atoms are trapped close to the vdW minima of the PES, with equal probabilities for sitting near one Br nucleus or the other one. The cylindrical symmetry of the molecular structures implies that the probability densities of L for the bent molecules (b) appear as two equivalent tori circulating about one or the other Br nuclei (lower panel). All heavy isotopomers BrLBr exist as linear (a) or bent (b) vdW structures. Here they are exemplified by BrDBr (a) and BrHBr (b).

quantum mechanical probability densities of the light atom (L) nuclei are trapped close to the vdW minima, with equal probabilities for sitting near one Br nucleus or the other. Accordingly, all the heavy isotopomers BrHBr, BrDBr, BrTBr, and Br^{4}HBr may be stabilized with two different vdW structures centered at the linear and bent vdW potential minima, only.

In contrast, linear BrMuBr is stabilized at the TS. The change from vdW bonding (Figure 3) to vibrational bonding (Figure 2) by isotopic substitution is the central result of this communication. The broad flat region in the domain of the saddle point has the effect of lowering the ZPE of the lightest isotopomer, BrMuBr, such that it is "trapped" in a vibrationally bound state, with a double-cone-type density distribution of the Mu atom centered at the TS, halfway between the two Br atoms (Figure 2).

In addition to the entirely different structures and localizations of vibrationally bonded BrMuBr at the TS versus the vdW-bonded heavy isotopomers of BrLBr in potential wells, Figures 2 and 3 also indicate entirely different mechanisms and energetics for the chemical bonding involved. Consider first the stabilization energy of the bent vdW structure exemplified by BrHBr in Figure 3b, 0.051 eV (= 0.163–0.112 eV). This is mainly due to the traditional gain of potential energy (0.059 eV) resulting from bond formation, at the expense of a small loss of ZPE (−0.008 eV); thus 0.051 eV also equals 0.059–0.008 eV.

Next consider the linear vdW-bonded structure exemplified by BrDBr in Figure 3a. Again the stabilization energy of 0.044 eV (= 0.117–0.073 eV) is driven by the gain in potential energy due to bond formation (0.053 eV), at the expense of a small amount of ZPE (−0.009 eV), leading to a similar result, 0.044 eV (= 0.053–0.009 eV). For the two vdW-bonded BrTBr and Br^{4}HBr radicals, almost the same values and sharing of stabilization energies are obtained (see Figure 4).

In contrast, the energy balance for vibrationally bonded BrMuBr is entirely different (Figure 2). Here though the stabilization energy 0.056 eV (= 0.481–0.425 eV) consists of the dominant gain of ZPE (= +0.342 eV) at the *expense* of potential energy (−0.286 eV). This complete reversal of the

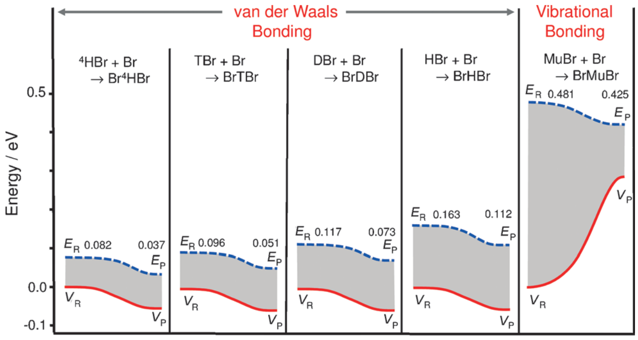

Figure 4. Van der Waals bonding of Br^{4}HBr, BrTBr, BrDBr, and BrHBr vs. vibrational bonding of BrMuBr. Each of the 4 + 1 panels shows the values of the potential energy (PE) V_R and V_P as well as the ground state energies E_R and E_P for the reactants (R) LBr + Br and for the products (P) BrLBr, adapted from Figures 2 and 3. The continuous red and dashed purple lines guide the eye from R to P. The gray-shaded gaps between these lines illustrate the variations in vibrational zero point energies (ZPEs), from R to P. The vdW bonding of the heavy isotopomers is due to the decrease in PE (first four panels). In contrast, vibrational bonding of BrMuBr results from the decrease of ZPE at the saddle point which overcompensates for the increase in PE (last panel).

roles of PE and ZPE means an unprecedented switch in the mechanism of chemical bonding due to isotopic substitution, as succinctly summarized in Figure 4. The principal result of this communication can be seen by comparing the last two panels in this figure. While the potential energy decreases from reactants (V_R) to products (V_P) for BrHBr upon the formation of a vdW-bound state (and for all heavier isotopomers), for BrMuBr it dramatically increases at the saddle point, but still there is a net gain in stabilization energy of 0.056 eV, arising from the ZPE difference between reactants and products.

The novel message of this communication is that isotopic substitution can change the nature of chemical bonding in a profound manner, from vdW bonding to vibrational bonding. This discovery means entirely different structures and symmetries and, most importantly, energetics and mechanisms of chemical bonding for different isotopomers of the heavy–light–heavy system discussed here. This conclusion is supported by a mosaic of complementary experimental results.[20–25] It should also help to stimulate searches for similar phenomena in other systems, including in similarly weakly bound vdW or hydrogen bonded molecules.

Computational Section

The ab initio potential energy surface for the ground-state BrHBr molecular system has been calculated at a multireference configuration interaction electronic structure level, with the augmented correlation consistent with a triple-zeta (aug-cc-pVTZ) basis set (MRCI + Q/AVTZ level of quantum chemistry), using the MOLPRO program code,[29] though without spin–orbit coupling. Comparisons with earlier more accurate quantum calculations in the region of van der Waals bound states for the HBr_2 system that do include spin–orbit coupling[27] show that its exclusion here is of only minor consequence in determining the binding energy of the BrMuBr vibrationally bonded state, which is the central result of this communication. Likewise, the results are robust with respect to non-Born–Oppenheimer corrections; for example, the finite difference approximation of the diagonal term yields a barrier reduction that supports vibrational bonding of BrMuBr even further, albeit by only 0.01 eV. We performed the above electronic structure calculations over 8000 geometries and a three-dimensional cubic spline interpolation was finally employed to yield a global potential energy surface (PES) for the system. Using this new global PES the resulting wavefunctions and energies of the ground states for all the isotopomers of the heavy–light–heavy molecule BrLBr, where L is an H atom isotope that varies from its lightest (muonium) to heaviest (muonic He[7,8]), are evaluated, using the method of Ref. [28]. For this purpose we have used the cylindrical coordinates (R,ρ,z), as in the quantum calculations of Ref. [21], where R is the Br–Br internuclear distance, with ρ and z representing the position of the central hydrogen atom or isotope in these coordinates. We performed three-dimensional evaluations of the wave functions using a discrete variable representation (DVR) method. For the R and z coordinates, standard particle-in-box basis sets were used while the radial portion of a two-dimensional harmonic oscillator was used for the ρ coordinate.

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