using high power pulsed lasers[33,34] is suitable for more conventional mass spectrometers in which ion-residence times are $\sim 10^{-6}$ s. Thus infrared photodissociation can be developed as a complementary technique to collisional activation for ion structure analysis. In particular, infrared excitation may be better suited to distinguish isomeric species because collision-induced dissociation of isomers often yields fragment ions in ratios that vary only slightly with the structure of the precursor ion.[2,35]

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Propensity Rules for Vibration-Induced Electron Detachment of Anions

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Abstract: Vibration-induced detachment of electrons from molecular anions has recently been experimentally observed. In this paper, the coupling of the anion's vibration–rotation motion to its electronic degrees of freedom is analyzed in an attempt to predict under what circumstances efficient detachment would be expected. A set of propensity rules based upon the shapes of the anion and neutral potential-energy surfaces is put forth and applied to several prototypical situations. The development is not aimed at permitting ab initio calculations of electron detachment rates. Rather, it is designed to provide a useful tool both for interpreting experimental data and for designing especially interesting experiments to carry out.

Recently it has been obsd.[1] that electrons can be detached from molecular anions by using infrared (IR) laser light to vibrationally excite the parent ions. The nature of the coupling between the nuclear motions, as excited by the IR light, and the electronic degrees of freedom has not been thoroughly analyzed. Analogous couplings which give rise to vibration-induced ionization of molecular Rydberg states have been analyzed by Berry and others.[2] Clearly what characterizes both anions and Rydberg states in this perspective is that the amount of energy required to cause ionization is often substantially less than the dissociation energies of bonds in the parent species. Such vibration-induced ionization would not be expected to occur for the ground states of most neutral molecules (e.g., for ethylene the lowest ionization potential is 10.5 eV, whereas the C–H bond energy is only 4.2 eV).

The primary purposes of the present manuscript are to (1) describe a physical mechanism which gives rise to the conversion of intramolecular vibrational (and/or rotational) energy into electronic energy, (2) give an expression for the electron-detachment rate which permits one to predict the propensity rules which govern these ionization events, and (3) make qualitative predictions concerning those anions which would or would not be expected to efficiently undergo vibration-induced electron detachment. The mathematical machinery used to express the rate of electron loss is not new to this development. It is the commonly employed non-Born Oppenheimer coupling picture[3] which Berry used[2] in an elegant fashion to provide insight into the autoionization lifetimes to Rydberg states. This manuscript is intended to analyze in chemical terms those factors which affect the rate of electron detachment so as to give a wide range of chemists an understanding of those circumstances under which molecular anions would be expected to autodetach upon excitation of their vibrational/rotational motion (either by heating or laser IR radiation or formation via exothermic chemical reaction).

Before beginning the quantum mechanical treatment of the coupling between the nuclear and electronic motions as it pertains to this autodetachment problem, it is useful to distinguish among several types of anion/neutral potential-energy surface juxtapositions which might arise. In Figures 1–5 we represent a few of the more likely arrangements of anion (A^-) and neutral (N) potential-energy surfaces as functions of some (unspecified at this time) geometrical coordinate Q. The features which distinguish among these surfaces are (1) whether or not the surfaces intersect at some value(s) of Q, (2) how rapidly the anion–neutral electronic energy difference varies with Q, and (3) whether the intersections of the two surfaces occur at the limits of Q (e.g., $R = 0$ or $R \to \infty$) or for some intermediate value of Q. The situation depicted in Figure 1 is likely to arise when the neutral's molecular orbital (ϕ) to which the "extra" electron is added is not bound for Q near the equilibrium geometry for the neutral but becomes bound as Q increases. Figures 2 and 3 might pertain to molecules whose lowest unoccupied molecular orbital (LUMO) is bound for all values of Q except perhaps (Figure 2) for Q at its extreme value. Figure 4 describes situations in which the binding energy of the neutral's LUMO varies strongly with Q, whereas in Figure 5 the electron affinity (EA) is weakly dependent upon Q, in which case the LUMO could be a nonbonding "passive" orbital.

For systems in which the anion and neutral potential surfaces actually intersect, there exists the possibility that when E^- lies *above* E^0 the anion's electronic state could undergo detachment by way of purely *electronic* shape or Feshbach mechanism[4] at a rate which is competitive with that of the mechanism discussed below. In this case, the anion state would have a nonzero width $\Gamma(Q)$ due to the electronic decay mechanism. The *total* rate of

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† Camille and Henry Dreyfus Fellow; John Simon Guggenheim Fellow.

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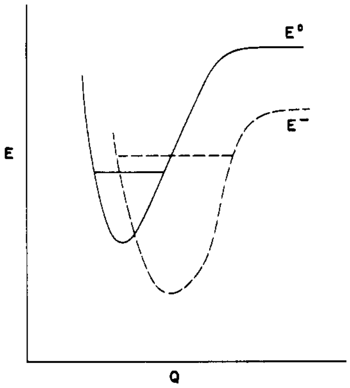

Figure 1. Anion and neutral potential-energy curves (as functions of an internal coordinate Q) appropriate to O_2^- and O_2.

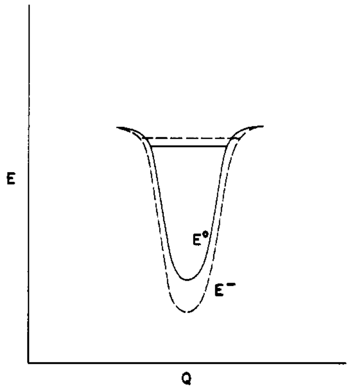

Figure 2. Anion and neutral potential-energy curves (as functions of an internal coordinate Q) appropriate to $PhCH_2^-$ and $PhCH_2$.

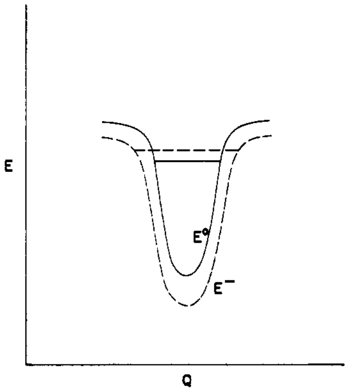

Figure 3. Anion and neutral potential-energy curves (as functions of an internal coordinate Q) appropriate to $PhNH^-$ and PhNH.

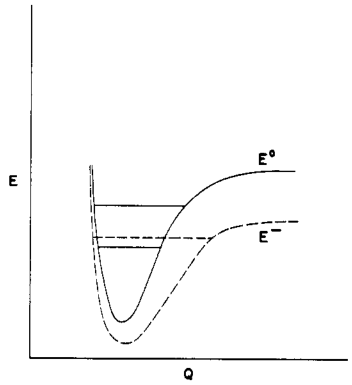

Figure 4. Anion and neutral potential-energy curves (as functions of an internal coordinate Q) appropriate to $LiCl^-$ and LiCl.

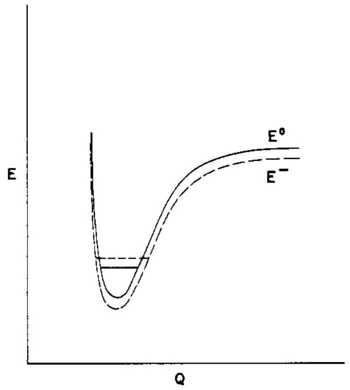

Figure 5. Anion and neutral potential-energy curves (as functions of an internal coordinate Q) appropriate to OH^- and OH.

electron detachment from the nth vibrational state of the anion could then involve the average of $\Gamma(Q)$ over this nth vibrational wave function's probability density plus the rate of loss from level n arising from the mechanism treated in this paper. The probability that the resultant neutral molecule is left in its n'th vibrational state would then be a weighted average of the rate of production of n' via the direct electronic process (which involves a conventional anion–neutral Franck–Condon factor) and the rate of production via the mechanism discussed here (which does not involve Franck–Condon factors). Therefore, in cases where both mechanisms are operative, the kinetic-energy distribution of the detached electrons, which reflects the anion–neutral vibrational-energy change distribution, would be described by a mixture of Franck–Condon and non-Franck–Condon terms. For the remainder of this work, we will restrict our attention to situations in which the purely electronic decay rate Γ is small enough (i.e., the anion is long lived *if* the nuclei are clamped) to guarantee that the rate of electron detachment is dominated by the "curve jumping" mechanism considered here. In a sense then, the electronic potential-energy curves which we are plotting are diabatic with respect to electron loss (i.e., the electron-detachment channel has been closed in "computing" E^- when $E^- > E^0$). For systems with nonnegligible values of Γ, the total rate of electron detachment would have to be interpreted as arising from both the mechanism treated here and the direct electronic mechanism (see Chen's work in ref 2).

In section of III of this paper, we shall describe specific molecular anions for which each of these potential-energy surface combinations is relevant. At that time we will also make predictions as to the relative rates with which anions typifying each of these "potential curve classes" should autoionize by way of the vibration–rotation-induced mechanism. Let us now briefly outline the quantum mechanical framework in terms of which the autodetachment rate is to be expressed.

I. Autodetachment Rate Expression

The simplest Hamiltonian which contains the relevant electronic and nuclear motion components can be expressed as follows:

$$\mathcal{H}(r,Q) = h(r|Q) - \sum_a \frac{\hbar^2}{2\mu_a} \nabla^2{}_{A_a} \tag{1}$$

where $h(r|Q)$ is the electronic Hamiltonian describing the motion of the $(N + 1)$ electrons in the presence of the nuclei *fixed* at positions $\{Q_a\}$, and $-[\hbar^2/(2\mu_a)]\nabla_{Q_a}{}^2$ is the kinetic-energy operator describing the motion of the nuclei along the Q_a "direction". $h(r|Q)$ thus contains the electronic kinetic energy plus the Coulombic potential energies of interaction among the electrons and nuclei. The coordinates of all of the electrons are collectively represented by r. The nuclear motion coordinates $\{Q_a\}$ correspond to all of the molecule's vibrational and rotational degrees of freedom.

The electronic potential-energy surfaces (E^- and E°) depicted in Figures 1–5 are assumed to be eigenfunctions of $h(r|Q)$.

$$h(r|Q)\psi_{A^-}(r|Q) = E^-(Q)\psi_{A^-}(r|Q) \tag{2}$$

$$h(r|Q)\psi_{Nk} = E^\circ(Q)\psi_{Nk} + [k^2\hbar^2/(2m)]\psi_{Nk} \tag{3}$$

The wave function ψ_{Nk} describes the neutral molecule N with electronic energy $E^0(Q)$ plus a free electron whose relative kinetic energy is $[\hbar^2/(2m)]k^2$ (m is the electron mass). Notice that $E^0(Q)$ and $E^-(Q)$ are assumed to be measured with respect to the same reference energy. The vibrational–rotational wave functions (χ_n^-, χ_n^0) which arise from the motion of the nuclei on each of these (adiabatic) electronic potential-energy surfaces obey

$$(-D_Q^2 + E^-)\chi_n^- = \epsilon_n^-\chi_n^- \tag{4}$$

and

$$(-D_Q^2 + E^0)\chi_n^0 = \epsilon_n^0\chi_n^0 \tag{5}$$

where D_Q^2 is simply our shorthand notation for the nuclear kinetic-energy operator appearing in eq 1 and $\{\epsilon_n^-,\epsilon_n^0\}$ are the anion and neutral molecule vibrational–rotational energies.

The electronic and nuclear motion product wave functions $\psi_{\mathrm{A^-}}\chi_n^-$ and $\psi_{\mathrm{Nk}}\chi_{n'}^0$ are not exact eigenfunctions of the full Hamiltonian of eq 1 because $\psi_{\mathrm{A^-}}$ and ψ_{Nk} depend upon Q, and hence $-D_Q^2$ operates not just on the χ_n^- and χ_n^0. As a result, the effect of nuclear motion (embodied in $-D_Q^2$) on the electronic wave functions $\psi_{\mathrm{A^-}}$ and ψ_{Nk} gives rise to a mixing or coupling between the two components ($\psi_{\mathrm{A^-}}\chi_n^-$ and $\psi_{\mathrm{Nk}}\chi_{n'}^0$) of the correct eigenfunction of H. This coupling can thus be viewed as giving rise to transitions between the anion and neutral molecule (plus free electron) states. To obtain an expression for this autodetachment rate ($W_{n\to n'}$), we employ the usual "Fermi (or Wentzel) Golden rule" result[5] of first-order time-dependent perturbation theory:

$$W_{n\to n'} = (2\pi/\hbar)|V_{\mathrm{Nk},n';\mathrm{A^-},n}|^2\rho_e(\epsilon_n^- - \epsilon_{n'}^0) \tag{6}$$

Here ρ_e is the density of translational states of the detached electron having kinetic energy equal to $\epsilon_n^- - \epsilon_{n'}^0$ and $V_{\mathrm{Nk},n',\mathrm{A^-},n}$ is the non-Born–Oppenheimer coupling matrix element discussed above.

$$V_{\mathrm{Nk},n';\mathrm{A^-},n} = \int \psi_{\mathrm{Nk}}^*\chi_{n'}^{0*}[\chi_{\mathrm{n}}^- D_Q^2\psi_{\mathrm{A^-}} + 2(D_Q\chi_{\mathrm{n}}^-)(D_Q\psi_{\mathrm{A^-}})]\,\mathrm{d}r\,\mathrm{d}Q \tag{7}$$

Because $\rho_e(E)$ is an increasing function of E

$$\rho_e(E) = (8m/h^2)^{3/2}(\pi/4)\sqrt{E} \tag{8}$$

anion-to-neutral transitions which yield high energy electrons tend to be favored by this term. However, because of the rather weak E dependence of ρ_e, it is more likely that the propensity rules governing such transitions arise from the variation of the V matrix element given in eq 7. Hence, we now turn our attention to the task of analyzing the physical content of eq 6 and 7 so that we may attain more insight into which transitions ($n \to n'$) are likely to be favored. Such knowledge would then permit one either to predict the distribution of the autodetached electron kinetic energies or to know what incident electron kinetic energies would be most efficient at forming anions in state ($\psi_{\mathrm{A^-}}\chi_n^-$ from neutrals in $\psi_{\mathrm{Nk}}\chi_{n'}^0$.

II. Propensity Rules

There are two distinct kinds of terms in eq 7. To gain some feeling for the sizes of these terms, we note that the *nuclear* kinetic energy operator $-[\hbar^2/(2\mu_a)]\nabla^2_{Q_a}$, when operating on the electronic wave function $\psi_{\mathrm{A^-}}(r|Q)$, yields a result which is proportional to m/μ_a times the result of the *electronic* kinetic-energy operator $[-(\hbar^2/2m)\nabla_r^2]$ operating on the same $\psi_{\mathrm{A^-}}$. Hence the electronic integral ($\int\psi_{\mathrm{Nk}}^*\nabla^2_{Q_a}\psi_{\mathrm{A^-}}\mathrm{d}r$) in the first term on the right-hand side of eq 7 is expected to be reduced by $(m/\mu_a)^{1/2}$ relative to the analogous integral ($\int\psi_{\mathrm{Nk}}^*\nabla_{Q_a}\psi_{\mathrm{A^-}}\mathrm{d}r$) in the second term. Although there are circumstances (e.g., when symmetry forces the second term to vanish) that the first term is larger, this is unusual. Hence, we now restrict our attention to the second term's (presumed) larger contribution to the V matrix element. Analysis of the first term can be carried through in analogous fashion, but doing so will not contribute further insight into the physical picture put forth here.

A more easily interpreted expression for the remaining term in V can be obtained by differentiating eq 2, with respect to Q_a to permit $D_Q\psi_{\mathrm{A^-}}$ to be reexpressed. Such differentiation, when followed by left multiplication by ψ_{Nk}^* and integration over the electronic coordinates yields

$$\left(E^0 + \frac{\hbar^2k^2}{2m}\right)\int\psi_{\mathrm{Nk}}^*\nabla_{Q_a}\psi_{\mathrm{A^-}}\,\mathrm{d}r + \int\psi_{\mathrm{Nk}}^*(\nabla_{Q_a}h)\psi_{\mathrm{A^-}}\,\mathrm{d}r = E^-\int\psi_{\mathrm{Nk}}^*\nabla_{Q_a}\psi_{\mathrm{A^-}}\,\mathrm{d}r \tag{9}$$

Solving this equation for $\int\psi_{\mathrm{N},k}^*\nabla_{Q_a}\psi_{\mathrm{A^-}}\mathrm{d}r$ and substituting into eq 7 results in

$$V_{\mathrm{Nk},n';\mathrm{A^-},n} = 2\int\chi_{n'}^{0*}\left[E^- - E^0 - \frac{\hbar^2k^2}{2m}\right]^{-1}\int\psi_{\mathrm{Nk}}^*(\nabla_{Q_a}h)\psi_{\mathrm{A^-}}\,\mathrm{d}r\nabla_{Q_a}\chi_n^-\,\mathrm{d}Q \tag{10}$$

This result is our final expression in terms of which we will now develop the propensity rules for vibration–rotation-induced electron detachment.

The integral connecting the bound anion state $\psi_{\mathrm{A^-}}$ to the continuum state ψ_{Nk} involves the electronic force operator $\nabla_{Q_a}h$. The derivative of the electronic Hamiltonian h with respect to a nuclear displacement along Q_a gives the force exerted on the electrons due to this displacement. One expects this integral to be large if there exist regions of Q space when the force operator is large and where a distortion (bond stretch, functional group rotation, etc.) of the molecular framework gives rise to a change in the highest occupied molecular orbital (HOMO) of the anion which results in this distorted HOMO having a large overlap with the continuum orbital whose de Broglie wavelength (λ) is given by $\lambda = 2\pi/k$ and $\hbar^2k^2/(2m) = \epsilon_n^- - \epsilon_{n'}^0$. For example, if $\epsilon_n^- - \epsilon_{n'}^0$ is small, so that the detached electrons have small kinetic energy and small momentum ($\hbar k$), then λ is large and efficient detachment will (possibly) occur if the nuclear displacement along Q_a makes the anion's HOMO very diffuse (so that its radial extent is of the order of λ).

The electronic matrix element $\int\psi_{\mathrm{Nk}}^*(\nabla_{Q_a}h)\psi_{\mathrm{A^-}}\mathrm{d}r$ of the force operator $\nabla_{Q_a}h$ has been approximated[2,6] in terms of an orbital-level integral involving the change in the potential felt by the extra electron due to motion of the nuclei and the charge density of the target's N electrons. The resultant integral $\int\phi_k^*[\nabla_{Q_a}V_{\mathrm{eff}}(r,Q)]\phi_{\mathrm{HOMO}}\mathrm{d}r$ expresses the transition from the anion's HOMO to the continuum orbital with wave vector $\hbar k$ caused by the gradient along Q_a of the electron–molecule effective potential V_{eff}. This potential contains the usual Hartree–Fock potential (which has local valence, exchange, and charge–dipole components) plus the charge-induced dipole, etc., potentials. Thus $\nabla_{Q_a}V_{\mathrm{eff}}$ gives the changes in all of these multipole potentials which accompany a distortion along Q_a.

The "energy denominator" appearing in eq 10 plays an important role in determining when electron detachment can occur. The energy difference, which clearly depends *strongly* on Q, $E^0(Q) - E^-(Q)$ is the minimum energy required to remove an electron from the anion if the nuclei were held fixed at Q. It is the vertical detachment energy of the anion. Of course, $\hbar^2\mathrm{k}^2/(2\mathrm{m})$ is the kinetic energy imparted to the ejected electron, so $E^0 + \hbar^2\mathrm{k}^2/(2\mathrm{m}) - E^-$ is the change in the *electronic* energy of the system if the electron were to be ejected at Q. Because the electron's kinetic energy $\hbar^2k^2/(2m) = \epsilon_n^- - \epsilon_{n'}^0$ is related to the vibrational–rotational energies of the anion and molecule, this same energy denominator can be viewed in a different light; $E^0 + \hbar^2\mathrm{k}^2/(2\mathrm{m}) - E^-$ is also $\epsilon_n^- - E^- - (\epsilon_{n'}^0 - E^0)$ which is the change in the vibration–rotation *kinetic* energy in going from the anion ($\epsilon_n^- - E^-$) to the neutral ($\epsilon_{n'}^0 - E^0$) at Q. Clearly, for electron detachment to be efficient, this energy denominator must be small. Too large a value causes a small detachment rate because the nuclear kinetic

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[5] See L. I. Schiff, "Quantum Mechanics", 3rd ed., McGraw Hill, New York, 1968.

[6] J. C. Y. Chen, *Phys. Rev.*, *129*, 202 (1963).

energy and momentum is "asked" to undergo too large a change in going from the anion to the neutral. Thus, for any particular $\epsilon_n^- - \epsilon_{n'}^0$, $E^0 - E^-$ must be as small as possible. This means that the anion and neutral potential-energy curves must either come close or intersect. Given such a near or actual intersection, small values of $\epsilon_n^- - \epsilon_{n'}^0$ will be preferred. For diffuse orbitals of anions or Rydberg orbitals of excited neutrals, the radial size of the orbital may range from 2 to 2000 Å. Hence k ranges from 3×10^8 to 3×10^5 cm^{-1} and therefore $\epsilon_n^- - \epsilon_{n'}^0$ ranges from 3×10^5 to 3×10^{-1} cm^{-1}. The former energy difference (3×10^5 cm^{-1}) is so large that such transitions are not very likely; the energy denominator factor, which is $[-\epsilon_n^- + \epsilon_{n'}^0 + E^- - E^0]^{-1}$ will be *at least* 3×10^{-6} (cm^{-1})$^{-1}$ for such processes. The transitions involving much more diffuse orbitals are more probable, since they correspond to smaller $\epsilon_n^- - \epsilon_{n'}^0$ factors and hence smaller energy denominators.

Finally, the integral over the nuclear displacements arising in eq 10 can significantly affect the state-specific detachment rates. On the basis of the above discussion, we conclude that the large contributions to the integrand will occur in regions of Q space where the energy denominator is small if the product $\psi_{n'}^{0*}\nabla_{Q_a}\chi_n^-$ is also large at these same Q values. To give a qualitatively correct account of the conditions under which this product is likely to be large, we point out that $\nabla_{Q_a}\chi_n^-$ would be proportional to $\chi_{n\pm1}^-$ if χ_n^- were a simple harmonic oscillator wave function involving the coordinate Q_a. In that case, $\chi_{n'}^{0*}\nabla_{Q_a}\chi_n^-$ is likely to be largest if $\chi_{n'}^0$ and χ_n^- involve motion along the same displacement coordinate and if the overlap of $\chi_{n'}^0$ and $\chi_{n\pm1}^-$ is large. However, the Schwarz inequality tells us that the overlap between $\chi_{n'}^0$ and $\chi_{n\pm1}^-$ is bounded by unity. Therefore it is probably more reliable to consider the effects of the energy denominator as dominant and then treat the product $\chi_{n'}^0\nabla_{Q_a}\chi_n^-$ at the position(s) Q where the energy denominator is smallest. Once the regions of Q space over which the energy denominator is small are identified, the product $\chi_{n'}^0\nabla_{Q_a}\chi_n^-$ (which may be approximately related to the product $\chi_{n'}^{0*}\chi_{n\pm1}^-$) can be evaluated at these Q values. One thus expects to find efficient transitions between $\chi_{n\pm1}^-$ and $\chi_{n'}^0$ only if (1) both $\chi_{n\pm1}^-$ and $\chi_{n'}^0$ are nonvanishing in regions of nuclear configuration space (Q space) where the potential-energy surfaces come close or intersect and (2) $\epsilon_n^- - \epsilon_n^0 = \hbar^2k^2/(2m)$ gives an outgoing electron of low kinetic energy which has high overlap with the anion's HOMO. Notice that the dominance of the energy denominator factor in determining the Q dependence of the integrand in $V_{Nk,n';A^-,n}$ gives rise to a dependence on χ_n^- and $\chi_{n'}^0$ which is not at all like the Franck–Condon factor[7] which arises in direct photon-induced electron detachment. Such is less the case for autoionization of Rydberg states for which the neutral and (positive) ion electronic energy difference $E^0(Q) - E^+(Q)$ is nearly constant as Q varies about its equilibrium value.

In the above discussion we often make use of the fact that efficient electron detachment requires the potential curves E^- and E^0 to intersect or approach closely. It is, of course, important to ask "how close is close enough"? The so-called Massey criterion,[8] which has been widely used to judge when such nonadiabatic transitions are likely, states that transitions from χ_n^- to $\chi_{n'}^0$ (i.e., E^- to E^0) are unlikely unless

$$|\hbar v_a \int \psi_{Nk}^* \nabla_{Q_a} \psi_{A^-}\, dr\, [E^- - E^0]^{-1}| \gtrsim 1 \qquad (11)$$

Here $\vec{v}_a$ is the (classical) velocity of the nuclei along the Q_a direction. For situations where E^- and E^0 are quite *parallel* (e.g., Figure 3 or 5), $E^- - E^0$ is constant and $\hbar\vec{v}_a$ can be approximated by $[2(\epsilon_n^- - E^-)]^{1/2}$. Then using eq 9 and $\hbar^2k^2/(2m) = \epsilon_n^- - \epsilon_{n'}$, eq 11 reduces to

$$||E^- - E^0|^{-1}[2\mu(\epsilon_n^- - E^-)]^{1/2} \int \psi_{Nk}^*(\nabla_{Q_a}h)\psi_{A^-}\, dr\, [E^- - E^0 + \epsilon_{n'}^0 - \epsilon_n^-]^{-1}| \gtrsim 1 \qquad (12)$$

The left-hand side of this equation will be large if $|E^- - E^0|$ is small (close parallel curves), $\epsilon_n^- - E^-$ is large (not near the turning points of E^-), and $\epsilon_{n'}^0 - \epsilon_n^-$ is small (small vibrational energy change).

In the neighborhood of a surface intersection or near *crossing* (at $Q_{a,c}$), the energies E^- and E^0 can be approximated as linear functions of Q_a.

$$E^- = \frac{\partial E}{\partial Q_a}(Q_a - Q_{a,c}) \equiv F^-(Q_a - Q_{a,c})$$

$$E^0 = \frac{\partial E^0}{\partial Q_a}(Q_a - Q_{a,c}) \equiv F^0(Q_a - Q_{a,c}) \qquad (13)$$

where F^- and F^0 are the forces felt by the nuclear framework due to a displacement along Q_a. If the coordinate Q_a is started (at $t = 0$) at $Q_{a,c}$ with velocity $\vec{v}_a$, a transition to E^0 will take place within one vibrational period ($\hbar/\epsilon_n^-$) of the mode along Q_a with good probability if eq 11 is obeyed. Using eq 13 and saying that, in the neighborhood of the (near) crossing,

$$Q_a(t) = Q_{a,c} + \Delta t \vec{v}_a \qquad (14)$$

eq 11 becomes

$$|\hbar \vec{v}_a \int \psi_{Nk}^* \nabla_{Q_a} \psi_{A^-}\, dr\, [(F^- - F^0)\Delta t v_a]^{-1}| \gtrsim 1 \qquad (15)$$

Canceling the $\vec{v}_a$, using eq 9, and $\Delta t = \hbar/\epsilon_n^-$ this result reduces to

$$|\epsilon_n^- \int \psi_{Nk}^*(\nabla_{Q_a}h)\psi_{A^-}\, dr \left(E^- - E^0 - \frac{\hbar^2k^2}{2m}\right)^{-1} (F^- - F^0)^{-1}| \gtrsim 1 \qquad (16)$$

Finally, making use of $\hbar^2k^2/(2\text{m}) = \epsilon_n^- - \epsilon_{n'}^0$ and evaluating eq 16 at $Q_a = Q_{a,c}$ (after the vibration has had time to make one oscillation), we obtain

$$|\int \psi_{Nk}^*(\nabla_{Q_a}h)\psi_{A^-}\, dr\, (F^- - F^0)^{-1}| \gtrsim \left|\frac{\epsilon_n^- - \epsilon_{n'}^0}{\epsilon_n^-}\right| \qquad (17)$$

This equation states that the electronic force ($\int \psi_{Nk}^*(\nabla_{Q_a}h)\psi_{A^-} dr$) caused by a displacement of Q_a divided by the change ($F^- - F^0$) in the force felt by the nuclear framework must be larger than the vibrational-energy change ($\epsilon_n^- - \epsilon_{n'}^0$) divided by the initial vibrational energy (ϵ_n^-) if efficient transitions from χ_n^- to $\chi_{n'}^0$ are to be expected. Therefore, near degeneracy of the vibrational levels ϵ_n^- and $\epsilon_{n'}^0$ and small changes in the slopes ($F^- - F^0$) of the potential surfaces at crossings or near crossings should make detachment efficient. In addition, high velocity of the nuclei (large $\vec{v}_a$ or large $\epsilon_n^-/\hbar$) and large changes in the multipole moments of the neutral's charge density with vibration along Q_a (i.e., large electronic forces) give rise to efficient detachment. Therefore, it is not only how close the potential surfaces approach but how they approach (e.g., with similar slope, etc.) which is just as crucial.

In summary, we have put forth the following set of propensity rules which should govern vibration–rotation-induced electron detachment processes: Specific transitions between χ_n^- and $\chi_{n'}^0$ will occur efficiently if (1) the anion and neutral potential energy surfaces (E^- and E^0) approach or intersect one another in regions of Q space where both $\chi_{n'}^0$ and $\chi_{n\pm1}^-$ are nonvanishing and the electronic force operator ($\nabla_{Q_a}h$) is large; (2) the change in slope $|F^- - F^0|$ in going from one potential curve to the other is small; (3) $\epsilon_n^- - \epsilon_{n'}^0 = \hbar^2k^2/(2m)$ is small and corresponds to a de Broglie wavelength ($\lambda = 2\pi/k$) for the outgoing electron which is of the order of the radial size of the anion's HOMO.

It should be stressed oncc again that these propensity rules apply only to transitions which arise via the vibration-induced mechanism discussed here. If the direct electronic (shape or Feshbach) mechanism is also operative, one expects vibrational propensities which involve Franck–Condon factors to also contribute. In fact, by experimentally measuring the vibrational transition propensities (which are related through $\hbar^2k^2/(2m) = \epsilon_n^- - \epsilon_{n'}^0$ to the kinetic-energy distribution of the detached electrons) one should be able to determine whether the electronic detachment route or the surface jumping route treated here is dominant in particular

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systems. In addition, once the system reaches a region of Q space in which the difference between E^0 and E^- is smaller than the energy of the quantum of light used in the experiment, direct photon-induced detachment can also occur.

It is possible to formulate the coupled electronic and vibrational-rotational motion problem for anion/neutral surfaces which actually penetrate in terms of an electronically adiabatic picture. This alternative formulation would, of course, be identical with the above treatment for systems whose curves do not cross (e.g., those described in Figures 2, 3 and 5). Because such an adiabatic treatment might shed further light on the physical basis of the detachment process and because it might be viewed as being more applicable to species which do not have long lifetimes (small Γ) when E^- lies above E^0, we now briefly outline its development.

The electronically adiabatic potential-energy curves applicable to a system such as that depicted in Figure 1 are $E_- \equiv \{E^-$ for $R \geq R_c$; E^0 for $R < R_c\}$ and $E_+ = \{E^0$ for all $R\}$, where R_c is the crossing point. The adiabatic electronic wave functions are $\psi_- \equiv \{\psi_{A^-}, R \geq R_c; \psi_{N,k=0} R < R_c\}$ and $\psi_+ \equiv \psi_{Nk}$ for all R. Here $\psi_{N,k=0}$ is a neutral molecule wave function multiplied by, and antisymmetrized with, a $k = 0$ continuum orbital for the extra electron. The vibration–rotation eigenfunctions and energy levels $\{\chi_n^-, \epsilon_n^-; \chi_{n'}^0, \epsilon_{n'}^0\}$ now refer to the adiabatic surfaces $E_+(Q)$ and $E_-(Q)$.

The mathematical development leading to eq 10 would apply equally well to the adiabatic case under consideration now. However, when one begins to consider the electronic force matrix element $\int \psi_{Nk}^*(\nabla_{Q_a} h)\psi_{A^-} dr$ it must be realized that this integral is nonzero only for $Q > Q_c$ since $\psi_{A^-} = \psi_{N,k=0}$ (which would have a negligible integral with ψ_{Nk}, $(\hbar^2 k^2/(2m) = \epsilon_n^- - \epsilon_{n'}^0)$ for $Q < Q_c$. Hence only the $Q > Q_c$ regions of nuclear configuration space contribute to determining the propensity rules. In these regions $E_- = E^-$, $E_+ = E^0$, and $E^0 - E^- > 0$, and the qualitative development of the propensity rules given above remains valid. One might wonder whether the different vibrational eigenfunctions χ_n^-, which arise in this picture due to the use of the fully adiabatic potential energy surface (E_-), might give rise to different propensity predictions. Such is not the case because (1) the $\epsilon_{n'}^0$ are identical in both (diabatic and adiabatic) pictures (since $E_+ = E^0$ for all Q) and (2) the functional form of χ_n^- for $Q > Q_c$ (which, for the diabatic case, is the only part of χ_n^- appearing in eq 10) is determined (primarily) by the potential surface which applies to this $Q > Q_c$ region. Since $E_- = E^-$ for $Q > Q_c$, the functional forms of the diabatic and adiabatic χ_n^- will be the same when $Q > Q_c$. As a result then, the adiabatic and diabatic propensity predictions are expected to be identical. The two formulations simply represent two different ways of looking at the same phenomena.

III. Predictions for Specific Classes of Anions

Having now developed some general feeling for what governs the probability that excitation of the anion's vibration–rotation motion will result in electron detachment, let us now attempt to apply this insight to the classes of anion/neutral systems depicted in Figures 1–5.

The potential-energy surfaces shown in Figure 1 could apply[9] to O_2^-/O_2 (but not to N_2^- which has an electronic detachment lifetime of $\sim 10^{-14}$ s) if Q is identified as the bond length R or to[10] SF_6^-/SF_6 if Q is taken to be the (presumed) one "active" S–F bond stretch coordinate which leads to $SF_5 + F$ upon dissociation of SF_6. For such systems, we predict efficient detachment for vibrational levels of A^- and N which lie near the surface intersection point and which have small energy differences $\epsilon_n^- - \epsilon_{n'}^0$. The threshold for vibration–rotation-induced detachment, which occurs near the surface intersection, would occur at lower excitation energies than would the peak of the direct electronic photodetachment cross section. The latter process would be expected to be very inefficient near threshold because of the poor Franck–Condon factors between the lowest anion and neutral vibrational levels. Finally, neutral systems described by Figure 1 should efficiently attach low-energy electrons to produce anions in vibrational levels lying near the surface intersection.

Figures 2 and 3 might, for example, be used to describe the benzyl ($PhCH_2^-$) and anilide ($PhNH^-$) systems[11] when Q is identified, respectively, as the CH_2^- or NH^- torsion angle (and pyramidalization) which varies from 0 to 90° as the p orbital on CH_2^- or NH^- rotates from being in conjugation with the π orbitals of the phenyl group to a perpendicular conformation where the conjugation has been destroyed. The benzyl anion and radical (neutral) potential surfaces are shown to intersect at $\theta = 90°$ because nondelocalized alkyl radicals $R\dot{C}H_2$ are known to have zero (or very small) electron affinities. In contrast, because alkyl substituted amino radicals $R\dot{N}H$ are known to form stable anions (e.g., the electron affinities of alkyl amino radicals are $\sim$0.7 eV), the anion and neutral potential surfaces shown in Figure 3 do not intersect at $\theta = 90°$.

The propensity rules discussed earlier lead us to predict that $PhNH^-$ should not undergo efficient vibration–rotation-induced electron detachment for any combination $(\chi_n^-, \chi_{n'}^0)$ of its torsional vibrational energy levels. It's potential-energy curves never come close enough together, although they do become rather parallel (so that $F^- - F^0$ is small). This species would, of course, be expected to undergo direct electronic photodetachment with good $0 \rightarrow 0$ Franck–Condon factors. The benzyl anion (whose adiabatic electron affinity is 0.9 eV) is expected to detach electrons only when its upper (torsional) vibrational levels are populated (by heating, IR multiphonon absorption, or one-step overtone absorption). It is only these high χ_n^-, $\chi_{n'}^0$ levels which sample the regions of θ space where the anion and neutral surfaces approach one another or intersect.

The pairs of surfaces shown in Figures 4 and 5 could apply to the $LiCl^-/LiCl$ (or LiH^-/LiH) and OH^-/OH systems,[12] respectively. For OH^- the extra electron occupies a nonbonding π orbital which is localized on the oxygen center. Thus, as the OH bond length ($R = Q$) is varied, the electron affinity ($\sim$1.8 eV) changes very little for rather substantial changes in R. In contrast, the orbital in which the extra electron resides in $LiCl^-$ changes significantly as the LiCl bond is broken. For values of R near the equilibrium bond length, the $LiCl^-$ HOMO can be well described as a 2s2p σ-hybrid orbital on the lithium center which is polarized away from the negative chlorine center. As R approaches infinity, the HOMO becomes a 3p orbital centered on-the chlorine atom. This drastic change in the nature of the HOMO gives rise to large changes in the separation $(E^- - E^0)$ between the anion and neutral potential-energy curves (i.e., the electron affinities of LiCl and Cl are 0.61 and 3.6 eV, respectively). For OH^-, we predict that vibrational excitation will not be effective in bringing about electron detachment because the potential-energy curves never come close to one another. On the other hand, the system described in Figure 4 might be expected to undergo electron loss but only if the surfaces of the anion and neutral approach one another closely at R values for which $E^-(R)$ still lies below the dissociation limit of the anion. If the surface crossing lies above the dissociation energy of the anion,[13] then one would expect that population of higher and higher anion vibrational-rotation levels would preferentially lead to rupture of the bond, thus giving fragmentation (e.g., $LiCl^- \rightarrow Li + Cl^-$). On the other hand, a surface crossing which lies above the anion dissociation energy could provide a mechanism for electron loss when in collisions (e.g., $Cl^- + Li \rightarrow Cl + Li + e$). In such cases, we would expect efficient electron detachment to occur for collisions whose impact parameters (i.e., relative collisional angular momenta) lie within a narrow

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range about the value of R where the two curves intersect (R_c). The collisional energy at which detachment should take place would be given as $E^-(R_c) - D_e(BA^-)$, where D_e is the dissociation energy of BA^-. In such transitions between a continuum nuclear motion state of the anion and a bound or continuum nuclear motion state of the neutral, the above mathematical treatment must be modified to take into consideration the scattering nature of χ_n^-. However, the qualitative arguments advanced above should still remain valid.

Clearly there is a wide variety of physical processes involving electron loss induced by some kind of nuclear motion (vibration, rotation, or collisional impact). Autoionization of molecular Rydberg states, Penning ionization of electronically excited atoms or molecules, and vibration–rotation-induced detachment of anions and merely three special cases which are likely to be of wide interest to chemists. Because of the recent observation of electron detachment in benzyl anion caused by the absorption of IR radiation, it is timely to consider the quantum mechanical basis in terms of which one can understand such behavior. It is hoped that the three propensity rules given in section II of this paper will stimulate further experimental research into this problem. It is our feeling that work on diatomic molecular anions (where Q can only be the interatomic distance) should be examined first. For polyatomic molecules, the observation of vibration–induced detachment is more difficult to interpret because of the multidimensional nature of the anion and neutral potential-energy surfaces. By testing the model given here on diatomics or small polyatomics, one can determine its range of validity. Then, if this model is successful, it can be used to suggest and interpret experiments involving polyatomic species.

At present, the experimental methods[1] employed to study vibration-induced detachment do not permit the determination of the anion vibrational level ϵ_n^- from which one is detaching. The intense infrared laser light sources used probably populate high vibrational levels of many models of the anion. The pressure used in the ICR laser detachment experiments[1] are so low and the infrared radiative lifetimes so long ($\sim 10^{-3}$ s) that vibrationally excited anions cannot lose their energy. As a result, the laser pumping eventually excites, by a stepwise mechanism, vibrational levels which are high enough in energy to detach. If the laser fluence is high enough, the population of these higher vibrational levels will be maintained and *eventually* (although perhaps with slow rate) electrons will detach. Thus, the only control one has for indirectly determining which vibrational levels are detaching is the laser fluence. Clearly this situation is not entirely satisfactory, and much remains to be done in the way of experimental development.

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Structures and Properties of Organic Liquids: *n*-Alkyl Ethers and Their Conformational Equilibria[1]

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Abstract: Statistical mechanics simulations have been carried out for liquid dimethyl ether (DME) and methyl ethyl ether (MEE) at their boiling points and for liquid diethyl ether (DEE) at 25 °C. The intermolecular interactions were described by Coulomb and Lennard-Jones terms in the TIPS format. The internal rotations about the central CO bonds in the MEE and DEE monomers were also included, using potential functions derived from ab initio molecular orbital calculations. Optimization led to the interesting result that the dihedral angle for the gauche conformer in MEE occurs at ca. 85° in accord with electron diffraction data. A key finding is that the conformational equilibria for MEE and DEE are essentially unaffected by transfer from the gas phase to the pure liquids at the normal densities. The thermodynamic and detailed structural results for the liquids are also thoroughly analyzed. Excellent agreement is found with experiment for the computed heats of vaporization of all three liquids. A simulation of liquid DME under constant pressure conditions yielded a density within 4% of the experimental value which provides further support for the validity of the TIPS model. The liquids are disordered with high coordination numbers and no obvious repeating polymeric units. Trends in the structures and properties as a function of monomer size are discussed.

I. Introduction

The traditional quantum mechanical studies of organic theoreticians are applicable primarily to problems of structure and reactivity in the gas phase. The need for expanding the scope to condensed phases is apparent since most experimental organic chemistry is performed in solution and because solvent effects are often profound. Consequently, a theoretical program for the systematic investigation of organic chemistry in the liquid state has been undertaken in this laboratory. Much of the initial work has focused on the generation and suitability of the necessary intermolecular potential functions which are at the heart of statistical mechanics simulations of fluids. A set of transferable intermolecular potential functions (TIPS) has been obtained for water, alkanes, alcohols, ethers, and alkyl chlorides.[3-6] The TIPS have proven particularly successful in simulations of a variety of pure organic liquids including methanol,[4] ethanol,[5] *n*-butane,[6] and 1,2-dichloroethane (DCE).[6] The computed thermodynamic and structural data were found to be in good agreement with the available experimental results including X-ray and infrared data. The nature of the computations also provides additional detailed

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