3402 J. Am. Chem. Soc. 1984, 106, 3402–3407

Vibration-Induced Electron Detachment in Molecular Anions

P. K. Acharya, Rick A. Kendall, and Jack Simons*

Contribution from the Chemistry Department, University of Utah, Salt Lake City, Utah 84112.

Received December 15, 1983

Abstract: Fully ab initio theoretical simulations of the rates of electron ejection caused by coupling between vibrational and electronic motion of molecular anions have been performed. These calculations are aimed at helping to interpret data of recent experiments in which anions are observed to undergo electron loss as they are excited via sequential infrared photon absorption. Two diatomic species, LiH^- and OH^-, were chosen for study because they represent good prototype systems for facile and slow electron ejection, respectively. Results of the present study show that 10^{-9}–10^{-10} s are required to "shake" an electron off LiH^- whereas OH^- requires 10^{-5}–10^{-6} s. These long-lived excited anion states may be observable as sharp features in photodetachment spectra. The molecular orbital out of which the electron is ejected is found to govern the overall ejection rate; the branching ratios for decay into vibrational levels of the neutral are strongly affected by quantal vibrational energy and momentum considerations. The ejection rates of all molecular anions that have been experimentally studied to date are thought to lie between the LiH^- and OH^- rates.

I. Introduction

What Is the Experimental Situation? Recent ion cyclotron resonance (ICR) experiments[1] of Brauman et al. and Beauchamp et al. indicate that vibrationally excited molecular anions (e.g., benzyl, allyl, enolates, anilide, 2,4-hexadienyl, and 1,3-cycloheptadienyl) undergo electron loss to yield corresponding neutral radicals. All of these anions have large enough electron affinities (>0.3 eV) to guarantee that at least three IR photons must be absorbed before electron ejection is possible. Pulsed infrared (IR) laser radiation in the fluence range 0.1–6 J/cm² is used by Brauman to vibrationally excite these anions which reside in an ICR cell in essentially collisionless conditions at $\sim 10^{-6}$ torr. Laser pulse times in the 1–3-μs range are commonly employed. The ICR ion signal (S) is found to decrease by an amount that depends upon the fluence output of the laser. Plots involving the ICR signal with (S) and without (S_0) the presence of the laser vs. fluence (F) are used[1] to extract phenomenological IR absorption cross sections (σ): $-\ln (S/S_0) = \sigma F$, which commonly range from 10^{-21}–10^{-19} cm². The loss of ion signal has been attributed[1,2] to electron ejection caused by intramolecular vibration-to-electronic (v–e) energy transfer.

It is useful to examine in a little more detail the implications of the experimental parameters mentioned above in an attempt to clarify how our theoretical work can help in the interpretation of the experimental data. We begin by comparing the rates of IR photon absorption, intramolecular vibrational energy redistribution, and v–e energy transfer. To do so, we compute the average number Φ of IR photons per cm² per s that impinge on the ICR cell given the fluence (F) in Joules/centimeter squared, the laser pulse duration (τ) in nanoseconds and the photon energy ($\bar{\lambda}$) in reciprocal centimeters: $\Phi = 5.03 \times 10^{31} F/(\bar{\lambda}\tau)$. Using $\bar{\tau} \sim 1000$ cm⁻¹, $\tau \sim 3000$ ns, and $F \sim 1.0$ J/cm², which are in line[3] with the experimental conditions of Brauman et al. in ref 1, one has $\Phi \sim 2 \times 10^{25}$ photons per cm² per s. This photon intensity, when mulitplied by a cross section σ describing the IR absorption process, gives the rate of photon absorption. Cross sections in the range $\sigma_F \sim 10^{-21}$–10^{-18} cm² are characteristic of fundamental vibrational transitions for neutral species. For ions in which the molecular vibration causes substantial changes in the electron distribution, the geometrical dipole derivative $\partial\mu/\partial R$ may be larger than for most neutrals, in which case σ_F could be larger by as much as a factor of 10–100. The cross sections that are obtained from the above mentioned plots of the logarithm of the ICR signal vs. laser fluence are characteristic not of any single fundamental IR transition. They have to do with the rate of sequential IR excitation of the ion and should be viewed as phenomenological parameters that characterize the rate-determining or slow steps in this multiple-photon IR excitation. Such cross sections are usually[1,4] found to be in the $\sigma_p \sim 10^{-21}$–10^{-19}-cm² range. An IR absorption cross section of 10^{-21}–10^{-18} cm² gives, when used with an earlier estimate of Φ, a photon absorption rate of $\Phi\sigma \sim (2 \times 10^4)$–$(2 \times 10^7)$ photons/s. Hence, the ICR experiments involve *sequential* vibrational excitations[3] spaced in time by $(\Phi\sigma)^{-1} \sim 50$–50 000 ns, which is much longer than the time (0.1–0.001 ns) needed for intramolecular vibrational energy redistribution. Hence, it is likely that, between photon absorptions, the energy is distributed among the vibrational and rotational modes of the anion even in the low-pressure ICR environment.

The above IR absorption rates together with the laser pulse time ($\sim$3000 ns) and the photon energy ($\sim$1000 cm⁻¹) allow us to estimate the average number of transitions that occur during the laser pulse. Using $\Phi \sim 10^{25}$ and $\sigma_F \sim 10^{-18}$ cm² gives $\sim$30 stepwise IR photon absorptions during the 3000-ns pulse. Phenomenological cross sections of $\sigma_p \sim 10^{-19}$–10^{-20} cm² translate into 0.3–3 transitions during the pulse. As mentioned earlier, in the latter case, the transitions must be interpreted as *net* transitions through the slowest step in the multiple-photon absorption process.

Because many IR photons may be absorbed during the laser pulse, there can be more than enough energy in the excited anions to detach electrons (electron affinities of the anions studied range from 0.3 to 2 eV) or to break chemical bonds. However, the rapid intramolecular energy redistribution makes it improbable that any one internal degree of freedom contains much more than its equipartition "share" of this energy at any instant of time. In fact, as Brauman et al. have recently demonstrated,[4] absorption of IR photons can continue even above the electron detachment threshold until electron detachment and bond rupture (which has a higher threshold energy) occur at competitive rates.

Statistical techniques[5] such as RRKM theory can be used to estimate how frequently any particular anion geometry is sampled given a specified total anion energy. However, as the above analysis of the rate of IR photon absorption indicates, uncertainties in the cross sections governing the vibrational transitions limit our ability to accurately specify the total energy content of the anions. If one were able both to *identify* those geometries near

---

[1] Meyer, F. K.; Jasinski, J. M.; Rosenfeld, R. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 663. Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1979**, *71*, 1030. Wight, C. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

[2] Simons, J. *J. Am. Chem. Soc.* **1981**, *103*, 3971.

[3] In the pulsed experiments of Brauman et al. Φ is not uniform during the entire pulse. During the first 200 ns of the laser pulse, Φ can be approximately 10 times higher than its value during the next 2800 ns. Hence, early in the laser pulse, IR photon absorption can be 10 times what we are about to calculate on the basis of an average (over 3000 ns) value of Φ.

[4] Foster, R. F.; Tumas, W.; Brauman, J. I. *J. Chem. Phys.* **1983**, *79*, 4644.

[5] See, for example: Johnston, H. S. "Gas Phase Reaction Rate Theory"; Roland Press: New York, 1966, Chapters 15 and 16.

0002-7863/84/1506-3402$01.50/0

which the v–e energy coupling is strong and to estimate the *rate* of v–e energy transfer, RRKM-like approaches might be used to test the v–e mechanism proposed in ref 1 and 2. Unfortunately, such a complete simulation of the ICR experiment is essentially impossible. Although we have some idea about the total energy E content of the anions studied in ref 1, the experimental method (IR sequential photon absorption) simply does not permit one to precisely determine E. Moreover, for polyatomic anions it is a formidable task to search the anion and neutral radical multidimensional potential energy surfaces for geometries where v–e coupling is significant (i.e., as will be seen later, where the anion and neutral potential energy surfaces approach each other).

Having pointed out the difficulties in carrying out theoretical studies on large molecules, we present, in this paper, results of thorough calculations on two diatomic anions (LiH$^-$ and OH$^-$) that should help in interpreting the autoejection phenomena occurring in many types of anions. We present rates of electron autodetachment from various anion vibrational levels to all of the energetically possible levels of the neutral, and we examine the propensity rules that govern these transitions. We also point out further experiments that can be carried out in order to observe the electron detachment caused by v–e energy transfer in these molecules.

II. Theoretical Simulations of Ejection Rates

(1) Why LiH$^-$ and OH$^-$? Because of the severe difficulties involved in performing a full theoretical analysis of the v–e detachment process for polyatomic anions, we decided to undertake a study of two diatomic anion (LiH$^-$ and OH$^-$) that we view as *limiting cases* in the sense that v–e energy transfer should be very facile in LiH$^-$ and very slow in OH$^-$. We chose to work on diatomic species to eliminate uncertainty about the energy content of the active vibrational mode. LiH$^-$ was chosen because it has a small adiabatic detachment energy[6] (~0.3 eV) and because the energy and radial extent of its active orbital (a 3σ orbital that is sp hybridized and localized on the Li center directed away from the H center) are strongly affected by vibration of the highly polar Li–H bond. These facts make LiH$^-$ an excellent candidate for rapid v–e energy transfer and hence rapid electron ejection. OH$^-$ was chosen because it has a relatively large detachment energy[7] (~1.8 eV), and its active nonbonding π orbital is localized on the O center and is not strongly affected by motion of the O–H bond. Therefore, OH$^-$ is expected to yield small v–e coupling and slow ejection rates. Of course, the fact that OH$^-$ and LiH$^-$ contain only a few electrons also played an important role in our decision to use them as our limiting-case anions; they are small enough to permit decent ab initio quantum mechanical treatment.

(2) Autodetachment Rate Expression. An expression for the rate of electron loss by the vibrationally excited anion has been derived elsewhere.[2] Here we briefly outline the physical factors underlying the derivation, state the resulting equation, and move on to discuss in detail our findings on LiH$^-$ and OH$^-$.

For all of the species studied in the Brauman experiments, and for our prototype (LiH$^-$ and OH$^-$) species, the *electronic* energy of the anion (i.e., the anion's potential energy surface) lies below that of the radical for *all* geometries sampled during the anion's vibrational motion. Therefore, if the anion did not vibrate (i.e., within the clamped-nuclei picture which forms the starting point of the Born–Oppenheimer separation), its total energy would simply be its electronic energy and it would be energetically impossible for the anion to *spontaneously* shed an electron because the neutral's total energy (i.e., energy surface) would be higher than the anion's. As the anion vibrates it achieves a *total* energy (electronic plus vibration/rotation) which can, depending on its degree of vibrational excitation, be greater than at least the zero-point energy of the neutral. Once this occurs, it is possible, *if* a coupling or energy-sharing mechanism exists between the vibrational and electronic degrees of freedom, for the anion to eject an electron. Hence, the autodetachment process being studied here is to be viewed[2] as a transition from a vibrational state of the anion to a vibrational state of the neutral species plus a free electron *caused* by vibration–electronic energy coupling.

The autodetachment process that we are addressing here can be thought of[2] as a transition between two Born–Oppenheimer vibronic states: $\chi_v^-\psi^- \rightarrow \chi_{v'}^0\psi_k^0$. Here χ_v^- and ψ^- denote the vibrational (with quantum number v) and electronic states of the anion, and $\chi_{v'}^0$ and ψ_k^0 denote the vibrational (quantum number v') and the electronic states of the neutral plus the free electron. The matrix element that couples the states between which the ejection process occurs was shown in ref 2 to be given by

$$V_{\mathrm{if}} = -\frac{\hbar^2}{2\mu}\int\int(\chi_{v'}^0\psi_k^0)^*[2\nabla_{\vec{Q}}\chi_v^-\cdot\nabla_{\vec{Q}}\psi^- + \chi_v^-\nabla_{\vec{Q}}^2\psi^-]\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{Q} \tag{1}$$

where μ is the appropriate "reduced" mass, $\vec{Q}$ denotes the coordinate along which the vibration occurs, and $\vec{r}$ denotes all of the electronic coordinates.[8] The vibrational eigenfunctions ($\chi_v^-,\chi_{v'}^0$) are functions of $\vec{Q}$, and the electronic eigenfunctions (ψ^-,ψ_k^0) are functions of $\vec{r}$ and possess a parametric dependence on $\vec{Q}$. The nuclear kinetic energy operator $-(\hbar^2/2\mu)\nabla_{\vec{Q}}^2$, when operating on the electronic wavefunction $\psi^-(\vec{r}|\vec{Q})$, yields a result that is proportional to m_e/μ times the result of the electronic kinetic energy operator $-(\hbar^2/2m_e)\nabla_{\vec{r}}^2$ operating on the same ψ^-. Hence the electronic integral $\int\psi_k^{0*}\nabla_{\vec{Q}}^2\psi^-\,\mathrm{d}\vec{r}$ in the second term on the right side of eq 1 is expected to be reduced by $(m_e/\mu)^{1/2}$ relative to the analogous integral $\int\psi_k^{0*}\nabla_{\vec{Q}}\psi^-\,\mathrm{d}\vec{r}$ in the first term in eq 1. Our calculations show that for fast transitions of LiH$^-$ (e.g., $v = 4 \rightarrow v' = 1$ and $v = 3 \rightarrow v' = 0$) the ratios of the contributions due *only* to the $\nabla_{\vec{Q}}^2$ term to those due *only* to the $\nabla_{\vec{Q}}$ term are ~0.001, and for slower transitions (e.g., $v = 10$ to $v' = 0$) this ratio is ~0.003. We shall, therefore, drop the second term in eq 1 in our further analysis.

The rate of transition between $\chi_v^-\psi^-$ and $\chi_{v'}^0\psi_k^0$ is given in ref 2 by $W = (2\pi/\hbar)|V_{\mathrm{if}}|^2\rho$, or

$$W = \frac{2\pi\hbar^3}{\mu^2}\left|\int\int(\chi_{v'}^0(\vec{Q})\psi_k^0(\vec{r}|\vec{Q}))^*\nabla_{\vec{Q}}\chi_v^-(\vec{Q})\cdot\nabla_{\vec{Q}}\psi^-(\vec{r}|\vec{Q})\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{Q}\right|^2\rho \tag{2}$$

where ρ denotes the density of translational states of the free electron confined to a very large cubic box of length L and energy $\hbar^2k^2/(2m_e)$

$$\rho = \frac{m_eL^3k}{2\pi^2\hbar^2} \tag{3}$$

Specialization of eq 2 to the case of the diatomic anions treated here is given below in eq 7.

(3) Computational Details. (A) Electronic Structure. In this section we describe how the above rate expression was implemented for the particular task of calculating OH$^-$ and LiH$^-$ autoejection rates.

The electronic wave functions for the anion ψ^- were taken to be the respective ($^2\Sigma$ for LiH$^-$ and $^1\Sigma$ for OH$^-$) Hartree–Fock Slater determinants. We assumed that for each neutral-plus-free-electron system, the electronic wave function could adequately be described by the same Slater determinant as for the anion except for the replacement of one spin–orbital. The active spin–orbital ($3\sigma\beta$ for LiH$^-$, $1\pi_x\beta$ for OH$^-$) of the anion ϕ_- was replaced by a continuum orbital ϕ_k describing the ejected electron. ϕ_k was approximated as a box-normalized (box-length L) plane wave $\exp(i\vec{k}\cdot\vec{r})$ which is orthogonalized to the occupied orbitals of the anion:

---

(6) Liu, B.; O-Ohata, K.; Kirby-Docken, K. *J. Chem. Phys.* **1977**, *67*, 1850. Jordan, K. D.; Griffing, K. M.; Kenney, J.; Andersen, E. L.; Simons, J. *Ibid.* **1976**, *64*, 4730. Jordan, K. D.; Luken, W. *Ibid.* **1976**, *64*, 2760.

(7) Hotop, H.; Patterson, T. A.; Lineberger, W. C. *J. Chem. Phys.* **1974**, *60*, 1809.

(8) Although angular derivative terms do, in principle, contribute to eq 1, their effects are expected to be small except for anions having very small electron affinities in which case the coupling of the rotational and electronic degrees of freedom can become significant. For the present situation (LiH$^-$ and OH$^-$) the electron affinities are larger than vibrational energies, so it is likely that v–e coupling is dominant.

$$\phi_k = (1/L^{3/2})[\exp(i\vec{k}\cdot\vec{r}) - \sum_{\substack{j=\text{occupied}\\ \text{in anion}}} \langle\phi_j|\exp(i\vec{k}\cdot\vec{r})\rangle\phi_j] \quad (4)$$

The kinetic energy of the plane wave is determined by the difference between the anion (ϵ_v^-) and neutral ($\epsilon_{v'}^0$) vibrational energies: $(\hbar^2k^2/2m_e) = \epsilon_v^- - \epsilon_{v'}^0$.

Clearly, we are employing a Koopman's theorem (KT) treatment of the electron detachment process. Such KT treatments of the electron affinity of LiH and the detachment energy of OH$^-$ are known[6,9] to yield qualitatively correct descriptions of the ion–neutral energy difference near the equilibrium geometry of the anion. We view the single-determinant treatment presented here as a reasonable approximation. Certainly, one could, and eventually should, move on to introduce correlated treatments of the anion and neutral species. However, we find (see our section III) that new insights and interesting results arise from even this approximate treatment of the electronic structure aspects of the ejection process.

Let us examine the nature of the orthogonalized plane wave for the LiH$^-$ and OH$^-$ cases. For LiH$^-$, we define the z axis to be the diatom's bond axis. Since the active orbital has σ symmetry ($m = 0$) and the result of applying the operator $\mathrm{d}/\mathrm{d}R$ does not change the σ symmetry, only those components of the orthogonalized plane wave that retain the σ symmetry contribute to the integral $\langle\phi_k|(\mathrm{d}3\sigma/\mathrm{d}R)\rangle$ which, as shown below in eq 7, arises in the ejection rate expression. The most general component $\phi_{k\sigma}$ of an orthogonalized plane wave having σ symmetry is obtained by projecting out of ϕ_k its $m = 0$ or z component. Thus $\phi_{k\sigma} = (1/2\pi)\int_0^{2\pi}\phi_k\,\mathrm{d}\alpha$, where α is the azimuthal coordinate of the $\vec{k}$ vector in spherical coordinates. This projection, when applied to the second group of terms in eq 4 simply picks out the σ orbitals in the sum over the anion's occupied orbitals. For the case in which the ejected electron's deBroglie wavelength is very long, i.e., $kr \leq 1$, it is straightforward to show that the σ-contribution of the orthogonalized plane wave is

$$\phi_{k\sigma} \approx (1/L^{3/2})[\exp(ik_zz) - \sum_{j=\sigma\,\text{only}} \langle\exp(i\vec{k}\cdot\vec{r})|\phi_j\rangle\phi_j] \quad (5)$$

where z and k_z are the z components of $\vec{r}$ and $\vec{k}$, respectively. For a typically strong LiH$^-$ to LiH + e transition, we find $k \approx 0.1$ bohr^{-1}. Therefore, for $r < 10$ bohrs, or about 3 times the bond length, one still has $kr < 1$. It is the above $\phi_{k\sigma}$ component of the general plane wave that should enter in our autodetachment rate expression. The total rates of electron ejection are obtained by integrating the expression for W of eq 2 over all orientations of $\vec{k}$ with respect to the z axis. However, since our calculations show that W is rather insensitive (because $kr < 1$) to the orientation of $\vec{k}$, we can simply take $\vec{k}$ to point along the z axis (from H to Li), in which case the integration over the direction of $\vec{k}$ gives a 4π factor that is already included in the density of states expression given in eq 3.

For OH$^-$ we again take the z axis to be the bond axis. We choose the active orbital to be the $1\pi_x$ molecular orbital, which consists mostly of p_x atomic orbitals on the oxygen center ($m = \pm1$). Projecting out of the orthogonalized plane wave of eq 5 its $m = \pm1$ components, we obtain the component of the plane wave that contributes to the ejection rate:

$$\phi_{k\pi} = \frac{1}{L^{3/2}2\pi}\Big[\Big(e^{-i\alpha}\int_0^{2\pi}e^{i\alpha}e^{i\vec{k}\cdot\vec{r}}\,\mathrm{d}\alpha + e^{i\alpha}\int_0^{2\pi}e^{-i\alpha}e^{i\vec{k}\cdot\vec{r}}\,\mathrm{d}\alpha\Big) - \sum_{j=\pi_+\pi_-}\langle\exp(i\vec{k}\cdot\vec{r})|\phi_j\rangle\phi_j\Big]$$

which, if we again assume $kr < 1$, gives

$$\approx\frac{1}{L^{3/2}}[(e^{ik_xx} - e^{ik_yy}) - \sum_{j=\pi_+,\pi_-}\langle\exp(i\vec{k}\cdot r)|\phi_j\rangle\phi_j] \quad (6)$$

For a typically strong OH$^-$ to OH + e transition, $k \approx 0.2$ bohr^{-1}. Therefore, in order that $kr < 1$, r must be less than $\approx$5 Bohrs or about $\approx$2.7 times the OH$^-$ bond length. When we use this expansion for $\phi_{k\pi}$ in our rate expression, the component $\exp(-ik_yy)$ along the y axis yield zero. Again considering the observed weak dependence of W on the direction of $\vec{k}$, we can replace the integration of W over various orientations of $\vec{k}$ by the value of W for k directed along the x axis. The density of states ρ given in eq 3 then again contains the appropriate 4π factor arising from the orientation integration for k.

The above approximation regarding the direction of $\vec{k}$ made the calculations a bit easier. If we do not make it, the quantitative results presented later would be somewhat different. Considering some transitions for LiH$^-$ as examples, the $v = 4 \rightarrow v' = 1$ and $v = 3 \rightarrow v' = 0$ (both fast transitions, $\approx 10^9$ s^{-1}) rates would have been ~2% and ~9% lower, and a slow transition such as $v = 10 \rightarrow v' = 0$ ($\approx 10^5$ s^{-1}) would have been ~60% lower. For these slow transitions, kr is not necessarily less than unity for all $\vec{r}$ values where the electronic integrand is significant. Since it is only the slow transition rates that are affected by our approximation, both the propensity rules deduced and the lifetimes given are essentially unaffected.

Using the Slater–Condon rules to evaluate the electronic integral appearing in eq 2, we can simplify the rate expression to one involving only the active anion orbital ϕ_- and the continuum orbital ϕ_k (orthogonalized plane waves $\phi_{k\sigma}$ or $\phi_{k\pi}$):

$$W = \frac{2\pi\hbar^3}{\mu^2}\left|\int\chi_{v'}^0(R)\int\phi_k^*(\vec{r},R)\,\frac{\mathrm{d}}{\mathrm{d}R}\,\phi_-(\vec{r},R)\,\mathrm{d}\vec{r}\,\frac{\mathrm{d}}{\mathrm{d}R}\,\chi_v^-(R)\,\mathrm{d}\vec{\mathrm{R}}\right|^2\rho \quad (7)$$

where R is the diatom's bond length. Notice that the L^3 factor appearing in ρ (eq 3) is cancelled by a factor of L^{-3} that arises from the normalization of ϕ_k as given in eq 4. This result, eq 7, is our final *working equation.*

The bound anion's active electronic orbital ϕ_- (3σ for LiH$^-$, 1π for OH$^-$) was evaluated as a linear combination of Gaussian-type atomic orbitals: $\phi_-(\vec{r},R) = \sum_jC_j(R)g_j(\vec{r},0) + \sum_jC_j'(R)g_j'(\vec{r},R)$ where the first sum consists of Gaussians g_j centered at the origin of the nuclear coordinate system (taken to be either the Li or O nucleus) and the second sum consists of Gaussians g_j' centerd on the H nucleus, which lies at a distance R from the first. The Gaussian basis sets employed were relatively large and were carefully chosen to provide a good description of the anion's diffuse charge density. The basis set used for LiH$^-$ was that used by Jordan[10] in his pioneering study of the binding of electrons to polar molecules. This basis set contains diffuse s and p orbitals on Li and a diffuse s orbital on H to ensure an accurate description of the anion's "extra" electron. For OH$^-$, we used the double ζ basis set of Basch et al. for oxygen[11] and the triple ζ basis set of Krishnan et al. for hydrogen[12] and added an additional diffuse p orbital on O and a polarization p orbital on H. The added basis function's exponents were optimized with respect to the total energy of OH$^-$. The LCAO-MO expansion coefficients $\{C_j(R)\}$ and $\{C_j'(R)\}$ were evaluated at numerous bond lengths using the Hartree–Fock self-consistent field procedure and then least-squares fit to polynomials in R. This fitting process then allows $(\mathrm{d}\phi_-/\mathrm{d}R)$ to be straightforwardly evaluated.

(B) Vibrational Wave Functions and Energies. Using highly accurate ab initio potential energy curves ($E^-(R)$ and $E^0(R)$) computed by Liu et al[6] for LiH$^-$ (who report Morse potential parameters of $D_e = 0.07717$ hartree, $\beta = 0.5480$ bohr^{-1}, and $R_e = 3.15$ bohr) and LiH ($D_e = 0.09242$ hartree, $\beta = 0.5971$ bohr^{-1}, and $R_e = 3.015$ bohr), we obtained the anion and neutral vibrational energies (ϵ_v^- and $\epsilon_{v'}^0$) and wave functions (and hence $(\mathrm{d}\chi_v^-/\mathrm{d}R)$) via numerical integration of the respective vibrational Schrödinger equations. For OH$^-$ and OH, spectroscopic data of Lineberger[7],[13] and others[9,13] were used to determine the parameters

---

(9) Smith, W. D.; Chen, T.-T.; Simons, J. *Chem. Phys. Lett.* **1974**, *27*, 499.

(10) Jordan, K. D. *Chem. Phys. Lett.* **1976**, *40*, 441.

(11) Basch, H.; Robin, M. B.; Kuebler, N. A. *J. Chem. Phys.* **1967**, *47*, 1201.

(12) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(13) Huber, K. P.; Herzberg, G. "Spectra of Diatomic Molecules"; Van Nostrand: New York, 1979. Kari, R. E.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1977**, *99*, 4539. Schulz, P. A.; Mead, R. D.; Jones, P. L.; Lineberger, W. C. *J. Chem. Phys.* **1982**, *77*, 1153.

Table I. LiH^- Detachment Rates (10^9 s^{-1}) and Lifetimes (10^{-10} s)[a]

v',v	Li–H bond length	3	4	5	6	7	8	9	10
0	*M*	7.17	2.21	0.532	0.115	0.0223	0.00372	0.00046	0.00002
	N	2.30	0.335	0.0244	0.00067	0.00160	0.00118	0.00052	0.00018
	P	0.146	0.0583	0.0346	0.0147	0.00344	0.00044	0.00002	0.00000
	P′	0.205	0.132	0.0504	0.0121	0.00126	0.00001	0.00004	0.00005
1	*M*		11.1	8.11	2.61	0.727	0.182	0.0404	0.00764
	N		4.83	1.61	0.203	0.00966	0.00555	0.00673	0.00401
	P		0.184	0.257	0.161	0.0859	0.0287	0.00579	0.00059
	P′		0.224	0.623	0.255	0.0840	0.0150	0.00081	0.00008
2	*M*				15.7	7.07	2.48	0.773	0.218
	N				4.04	0.795	0.0809	0.0116	0.0185
	P				0.491	0.470	0.273	0.121	0.0355
	P′				1.58	0.776	0.302	0.0811	0.0107
3	*M*					9.68	13.4	5.96	2.27
	N					3.34	1.96	0.340	0.0413
	P					0.142	1.03	0.658	0.342
	P′					1.17	1.83	0.770	0.273
4	*M*							15.1	10.9
	N							2.82	0.844
	P							1.24	1.34
	P′							2.75	1.61
lifetimes	*M*	1.39	0.751	1.16	0.543	0.571	0.622	0.457	0.747
	N	4.35	1.94	6.12	2.36	2.41	4.88	3.15	11.0
	P	68.5	41.3	34.3	15.0	14.3	7.51	4.94	5.82
	P′	48.8	28.1	14.9	5.41	4.92	4.66	2.78	5.28

[a] *N* denotes the equilibrium bond length (R_e = 1.595 Å) for LiH, and *M*, *P*, and *P′* denote LiH bond lengths of R_e − 0.050, R_e + 0.050, and R_e + 0.071 Å, respectively.

Table II. OH^- Detachment Rates (10^5 s^{-1}) and Lifetimes (10^{-6} s)[a]

v',v	O–H bond length	5	6	7	8	9	10	11
0	*M*	4.17	13.0	8.44	4.10	1.81	0.775	0.334
	N	0.649	1.36	0.554	0.152	0.0321	0.0048	0.0003
	P	0.0141	0.0018	0.0080	0.0181	0.0159	0.0100	0.0054
1	*M*			32.3	34.4	21.6	11.5	5.82
	N			3.97	2.84	1.12	0.345	0.0871
	P			0.0204	0.0079	0.0546	0.0715	0.0586
2	*M*				12.5	58.7	52.9	35.1
	N				1.79	5.96	3.67	1.59
	P				0.0183	0.0001	0.0561	0.131
3	*M*						27.8	65.4
	N						3.41	5.87
	P						0.0086	0.0123
lifetimes	*M*		0.769	0.245	0.196	0.122	0.108	0.0938
	N		7.35	2.21	2.09	1.41	1.35	1.32
	P		5587.0	352.0	226.0	142.0	68.4	48.2

[a] *N* denotes the equilibrium bond length (R_e = 0.9705 Å) for OH, and *M* and *P* denote OH bond lengths of R_e − 0.0164 and R_e + 0.0159 Å, respectively.

of the respective Morse potentials (for OH^-, D_e = 0.1830 hartree, β = 1.152 bohr^{-1}, and R_e = 1.822 bohr, and for OH, D_e = 0.1698 hartree, β = 1.214 bohr^{-1}, and R_e = 1.834 bohr) from which the vibrational energies and wave functions were obtained.

III. Discussion of Results of Theoretical Simulations of Ejection Rates

Given the anion and neutral electronic and vibrational wave functions and the requisite derivatives ($d\phi_-/dR$) and ($d\chi_v^-/dR$), we were able to evaluate the transition rates (*W*) for numerous LiH^- and OH^- ejection transitions. These rates are given in Tables I and II.

One immediately notices that the state-of-state LiH^- detachment rates ((2×10^5)–(4×10^9) s^{-1}) are generally higher than those for OH^- ((3×10^1)–(6×10^5) s^{-1}). The reciprocal of the sum of the rates of decay out of each anion level ϵ_v^- into all accessible neutral levels ϵ_v^0 determines the lifetimes of the ϵ_v^- level. The decay lifetimes (10^{-9}–10^{-10} s for LiH^- and 10^{-5}–10^{-6} s for OH^-) are *much* longer than the anion's fundamental vibration period (2.829×10^{-14} s for LiH^- and 9.033×10^{-15} s for OH^-). Thus, LiH^- must vibrate at least 7000 times before an electron is ejected; OH^- requires at least 10^8 vibrations. The primary origin of this large difference in lifetimes lies in the fact that the LiH^- 3σ orbital has a much stronger *R* dependence than does the 1π OH^- orbital (i.e., $d\phi_-/dR$ is larger for LiH^- than for OH^-).

The long lifetimes predicted for these vibrationally hot anions have implications for experiments designed to probe the v–e ejection process using overtone excitation to prepare the excited anion. The same photon used to vibrationally excite the anion (e.g., $\mathrm{LiH^-}$ ($v = 0$) + $h\nu \rightarrow \mathrm{LiH^-}$ ($v = 3$) can also directly detach the electron via an electric dipole transition (e.g., $\mathrm{LiH^-}$ ($v = 0$) + $h\nu \rightarrow$ LiH ($v' = 0$) + e). Cross sections for the photodetachment (direct) process are typically $\sim 10^{-17}$ cm^2 and are smoothly varying over energy ranges that are small with respect to the vibrational spacings of the neutral molecule. Fundamental infrared absorption cross sections for neutral species are $\sim 10^{-20}$ cm^2, and overtone transitions usually have intensities that are approximately 10 times smaller for each overtone order n. As noted earlier, IR cross sections for ions can be somewhat larger if the vibration involves large changes in the electron distribution (as it does for $\mathrm{LiH^-}$). Hence, the photodetachment spectrum is expected, near the photon energy corresponding to overtone excitation of the anion, to show a resonance feature with strength lower than that of the direct process. Because of the long lifetimes of the vibrationally excited $\mathrm{LiH^-}$ and $\mathrm{OH^-}$ anions, the widths of the resonance features are *not* Heisenberg limited. The intensity of the resonance feature is expected to be small relative to that of the direct photodetachment process (e.g., the intensity ratio for $\mathrm{LiH^-}$ ($v = 3$) $\rightarrow$ LiH ($v' = 0$) + e is $\sim 10^{-20}(0.1)^2/10^{-17} = 10^{-5}$, and for $\mathrm{OH^-}$ ($v = 5$) $\rightarrow$ OH ($v' = 0$) + e, it is $\sim 10^{-20}(0.1)^4/10^{-17} = 10^{-7}$). Hence, it will not be easy to detect[14] vibration-induced electron autodetachment by looking for resonance features in a direct photodetachment spectrum. At the risk of lowering the absolute signal intensities, one can better the above relative intensities by performing two-color experiments in which one laser is used to first excite the anions to, say, the $v = 2$ level, and then a second laser is used to effect both direct photodetachment and further vibrational excitation (e.g., $\mathrm{LiH^-}$ ($v = 0$) + $h\nu \rightarrow \mathrm{LiH^-}$ ($v = 2$) + $h\nu \rightarrow \mathrm{LiH^-}$ ($v = 3$) or LiH ($v' = 0$) + e). In this way one can cause the ratio of the ejection to direct detachment signals to be higher (e.g., $10^{-20}/10^{-17}$ for the above $\mathrm{LiH^-}$ example), but the absolute signal will decrease because of the sequential two-color excitation.

The data of Tables I and II also indicate that transitions that involve small energy changes are usually favored (e.g., $\mathrm{LiH^-}$ $v = 7$ decays at a much higher rate to $v' = 3$ LiH than to $v' = 0$, 1, or 2 LiH). To investigate the origins of these propensities, we performed a number of "model calculations" in which we modified the overlaps between the vibrational functions $\chi_{v'}{}^0$ and $(\mathrm{d}\chi_v{}^-/\mathrm{d}R)$. By shifting the LiH or OH equilibrium bond length, we vary only $\chi_{v'}{}^0$; $\epsilon_v{}^- - \epsilon_{v'}{}^0$, ϕ_k, and ϕ_- remain unchanged. We found that a 0.05-Å decrease in the LiH bond length gave rise to about a 10-fold increase in the various detachment rates. Increasing the LiH bond length resulted in lower detachment rates than those at the equilibrium bond length. However, this decrease in rate is not monotonic; see, for example, $\mathrm{LiH^-}$ ($v = 7$) $\rightarrow$ LiH ($v' = 3$) + e. For $\mathrm{OH^-}$, we found that a 0.016-Å increase (decrease) in the OH bond length gave rise to about a 10-fold decrease (increase) in the various detachment rates. We have also incorporated these data in Tables I and II. By shifting the relative equilibrium bond lengths (R_e) of the anion and neutral, we move the vibrational functions $\chi_{v'}{}^0$ and $(\mathrm{d}\chi_v{}^-/\mathrm{d}R)$ relative to one another. This then alters their phase relation and their overlap. Shifting the relative R_e's also changes the spacing between the anion (E^-) and neutral (E^0) potential energy curves. However, the E^0–E^- spacing and the $\chi_{v'}{}^0$, $(\mathrm{d}\chi_v{}^-/\mathrm{d}R)$ overlap are not independent, since the *local* shapes of $\chi_{v'}{}^0$ and $\chi_v{}^-$ are determined by the local vibrational kinetic energies $\epsilon_v{}^- - E^-(R)$ and $\epsilon_{v'}{}^0 - E^0(R)$, respectively. In ref 2, the rate expression (eq 2) has been recast in a form in which the potential energy spacing E^0–E^- appears explicitly. Although this rate expression is considerably more difficult to evaluate than the expression we have used, it does show that *one* of the major factors influencing the rate is the E^0–E^- spacing; the closer these curves approach each other, the greater the rate becomes.

We attempted to rationalize the observed relative propensities (for a given anion and neutral-plus-free-electron system) classically by considering energy and momentum conservation for the electron and vibrating molecular framework. Our approach was to find those points on the potential curve of the anion (say, of $\mathrm{LiH^-}$) where the total momentum of the system would be conserved if it made a vertical jump from the anion potential energy curve to the neutral curve. The change of the ejected electron's momentum was taken to be $(-\hbar k \pm (2m_e\mathrm{EA})^{1/2} \equiv \Delta p_e)$ and was directed along the z axis away from the Li nucleus. Here EA is the electron affinity of the neutral and enters because we approximate the active electron's momentum before ejection via the virial theorem.[15] The vibrational momentum of $\mathrm{LiH^-}$ before ejection was taken to be $\pm(2\mu(\epsilon_v{}^- - E^-(R)))^{1/2} = p_-$ and that of LiH after ejection to be $p_0 \equiv \pm(2\mu(\epsilon_v{}^0 - E^0(R)))^{1/2}$. Both are directed along the z axis. Taking the appropriate combination of plus or minus momenta (not all combinations are possible), we calculated the change in the momentum of the nuclear framework p_0–p_-. However, we found that at *no* values of R did this momentum change equal the ejected electron's momentum change. Thus, this simple classical model is not capable of yielding a qualitative description of the process. The electron seems to be too light to carry away enough momentum to permit this classical picture to be valid. Had we found R values ($R = R_c$), at which $\Delta p_e = p_0 - p_-$, it would have been reasonable to model the ejection rate W as follows:

$$W \propto \sum_{R_c} (|\chi_v{}^-(R_c)|^2 \,\mathrm{d}R)\left(\frac{p_-(R_c)}{\mathrm{d}R}\right) = \sum_{R_c} |\chi_v{}^-(R_c)|^2 (2\mu(\epsilon_v{}^- - E^-(R_c)))^{1/2} \quad (8)$$

Here the first factor in parentheses denotes the probability of $\mathrm{LiH^-}$ being between R_c and $R_c + \mathrm{d}R$, and the second factor in parentheses is proportional to the reciprocal of time spent by $\mathrm{LiH^-}$ between R_c and $R_c + \mathrm{d}R$, that is, to the rate of passage through $R = R_c$. However, it appears that such a simple classical approach cannot be invoked to explain even qualitatively the electron ejection process. We present this negative result here because it indicates that the propensities for electron ejection cannot straightforwardly be viewed in terms of classical energy and momentum conservation; quantum factors are obviously governing these propensities. These quantal constraints, as embodied in the relative phases of $\chi_{v'}{}^0$ and $(\mathrm{d}\chi_v{}^-/\mathrm{d}R)$, are most important in determining the propensities. The electronic details contained in the $\mathrm{d}\phi_-/\mathrm{d}R$ factors, dominate the *absolute* ejection rates. It should not be too surprising that the electronic factors are less important to the propensities because the ejected electrons' deBroglie wavelengths are at least 15 Å for all of the transitions studied here, as a result of which the integral $\int \phi_k{}^* (\mathrm{d}\phi_-/\mathrm{d}R)\, \mathrm{d}\vec{r}$ varies only weakly from one transition to another (for a given anion system).

IV. Concluding Remarks

Interpretation of the experimental data of Brauman et al. and of Beauchamp et al. presents challenges to the theoretician. Uncertainties regarding energy content of the anions excited by sequential IR photon absorption together with a large number of internal degrees of freedom combine to make a simulation of the v–e energy transfer mechanism for electron ejection impractical. To obtain a *range* of rates for v–e energy transfer that should cover most molecular anions that have been experimentally studied to date, we carried out a fully ab initio study of $\mathrm{LiH^-}$ and $\mathrm{OH^-}$. The lifetimes associated with electron loss of various $\mathrm{LiH^-}$ vibration levels (10^{-9}–10^{-10} s) were found to be much shorter than those for $\mathrm{OH^-}$ (10^{-5}–10^{-6} s). The origin of this rate difference for these "limiting case" anions lies in the dependence of the anions' active orbital on bond length (R); ϕ_- is much larger for the 3σ orbital of $\mathrm{LiH^-}$ than for the 1π orbital of $\mathrm{OH^-}$. Even the shortest lived $\mathrm{LiH^-}$ level has a Heisenberg width ($\sim$0.1 cm^{-1}) narrow enough to possibly allow observation of these decaying states as resonances in the anion's photodetachment spectrum.

The branching ratios for the production of various neutral vibrational states from a given anion vibrational level were found to be dominated by quantum mechanical vibrational phase factors

---

(14) W. C. Lineberger (private communication) has indicated that he is presently undertaking such experiments.

(15) Eyring, H.; Walter, J.; Kimball, G. E. "Quantum Chemistry"; Wiley: New York, 1944; p 357.

rather than by electronic details. Transitions to the energetically closest neutral vibrational level were generally found to be larger than those to other levels.

Our work aimed at understanding the multiple-photon ICR experiments is continuing. The computational data on LiH^- and OH^- provide us with a range of rates within which we expect most v–e ejection rates to fall. They also give some insight into how the electronic and vibrational factors affect the v–e rates and branching ratios. We are presently in the process of performing an ab initio simulation of the v–e ejection rate of the enolate H_2C^-COH, in which the torsion and "puckering" of the H_2C group is treated as the single active vibration.

Acknowledgment. We acknowledge the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant 8206845).

Registry No. LiH^-, 7580-67-8; OH^-, 14280-30-9.

Importance of Multicenter Integrals in Semiempirical Calculations of Nuclear Spin–Spin Coupling Constants. 1. Isotropic Coupling

J. C. Facelli[1] and M. Barfield*

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721.

Received July 14, 1983

Abstract: A study of Fermi contact, orbital, and spin-dipolar contributions to isotropic nuclear spin–spin coupling constants is presented in terms of a semiempirical (INDO) molecular orbital (MO) approach that extends existing theory to include all integrals for the three types of terms over Slater-type orbitals (STO's). All contributions are evaluated by the first-order polarization propagator approach (FOPPA), which is equivalent to the coupled Hartree–Fock (CHF) theory. Calculated coupling constant results for representative molecules are compared with experimental data, and reasonable correspondence is noted between these noncontact contributions and ab initio results with large Gaussian basis sets. Detailed comparisons are also made with semiempirical SCPT-MO results in the one-center integral approximation. Since the latter procedure leads to identically zero orbital and dipolar contributions if either one of the coupled nuclei is a proton, this extension of the theory is applicable to many very important types of coupling. For example, the calculated geminal and vicinal $^1H-^{19}F$ coupling constants, for which the OB and SD contributions are important, are in better conformity with the experimental data. It is now clear that the scaling of the one-center integrals for carbon far above the atomic Hartree–Fock values may be a consequence of the neglect of the multicenter integrals. The introduction of multicenter integrals into semiempirical methods greatly extends the number and the complexity of molecules for which contributions of all mechanisms can be investigated.

Theoretical studies of nuclear spin–spin coupling constants are extensive and have been the subject of several recent reviews.[2] Within the usual Ramsey perturbation formulation[3] the isotropic nuclear spin–spin coupling constant between nuclei N and N′ is written as the sum of four terms

$$J_{NN'} = J_{NN'}^{(1a)} + J_{NN'}^{(1b)} + J_{NN'}^{(2)} + J_{NN'}^{(3)} \qquad (1)$$

where $J_{NN'}^{(1a)}$ and $J_{NN'}^{(1b)}$ are the one- and two-electron orbital (OB) contributions, respectively,[4] $J_{NN'}^{(2)}$ is the spin-dipolar (SD) contribution, and $J_{NN'}^{(3)}$ denotes the Fermi contact (FC) contribution.[2,3] By far the largest number of calculations have been based on the finite perturbation theory (FPT) formulation in the intermediate neglect of differential overlap (INDO)[5] approximation of semiempirical MO theory. Only the Fermi contact (FC) term in eq 1 is included and, as usually carried out, the INDO-FPT method retains only the one-center integrals

$$\langle ns_N|\delta(r_N)|ns_N\rangle \equiv s_N^2(0) \qquad (2)$$

where ns_N denotes an s-type orbital at nucleus N. The empirical determination of $s_N^2(0)$ in a least-squares sense[5] from the experimental data compensates for a number of severe approximations.

Multicenter integrals (MCI) of the types $\langle\phi_B|\delta(r_A)|\phi_B\rangle$, $\langle\phi_A|\delta(r_A)|\phi_B\rangle$ and $\langle\phi_B|\delta(r_A)|\phi_C\rangle$, which are not included in the usual semiempirical calculations, have been discussed by several authors.[6-8] An important anomaly arises in zero differential overlap (ZDO) schemes, which use Slater-type orbitals (STO's) and neglect inner shell orbitals. Since electron densities $s_N^2(0)$ in eq 2 vanish identically for $n \geq 2$, only interproton coupling contributions to the Fermi contact term are rigorously nonvanishing (vide infra).

The next largest number of computations of nuclear spin–spin coupling constants is based on the self-consistent perturbation theory (SCPT) formulation,[9] which is an alternative coupled Hartree–Fock (CHF) scheme. This approach uses semiempirical MO theory but also includes algorithms for calculating the orbital (OB, $J_{NN'}^{(1b)}$ in eq 1) and spin-dipolar (SD, $J_{NN'}^{(2)}$ in eq 1) contributions. The one-center integral approximation is adopted with integrals of the type

---

(1) On leave from Department of Physics, University of Buenos Aires, with an External Fellowship of the Consejo Nacional de Investigaciones (CONICET, Argentina).

(2) Kowalewski, J. *Annu. Rep. NMR Spectrosc.* **1982**, *12*, 81; *Prog. Nucl. Magn. Reson. Spectrosc.* 1977, *11*, 1; *Spec. Period. Rep. Nucl. Magn. Reson.* **1982**, *11*, 55.

(3) Ramsey, N. F. *Phys. Rev.* **1953**, *91*, 303.

(4) The one-electron orbital terms $J_{NN'}^{(1a)}$ in eq 1 are not included in this study. These contributions have been estimated by numerical integration [Lee, W. S.; Schulman, J. M. *J. Chem. Phys.* **1979**, *70*, 1530. Matsuoka, O.; Aoyama, T. *Ibid.* **1981**, *73*, 5718] and analytical methods [Barfield, M.; Gottlieb, H. P. W., unpublished results, 1978–1979].

(5) Pople, J. A.; McIver, J. W., Jr.; Ostlund, N. S. *J. Chem. Phys.* **1968**, *49*, 2960, 2965.

(6) Varga, J. A.; Zumdahl, S. S. *Theor. Chim. Acta* **1971**, *21*, 211.

(7) Barbier, C.; Berthier, G. *Theor. Chim. Acta* **1969**, *14*, 71.

(8) Archirel, P.; Barbier, C. *J. Chim. Phys.-Chim. Biol.* **1978**, *75*, 1003.

(9) Blizzard, A. C.; Santry, D. P. *J. Chem. Phys.* **1971**, *55*, 950; **1973**, *58*, 4714.