

# Vibration-Induced Electron Ejection in Molecular Anions

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**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 interpreting data of recent experiments in which anions are observed to undergo electron loss as they are excited via sequential infrared photon absorption. Results of the present study show that  $10^{-9}$  -  $10^{-10}$  sec are required to "shake" an electron off  $\text{LiH}^-$  whereas  $\text{OH}^-$  requires  $10^{-5}$  -  $10^{-6}$  sec. These long lived excited anion states may be observed 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 vibrational energy and momentum considerations. The ejection rates of all molecular anions which have been experimentally studied to date are thought to lie between the  $\text{LiH}^-$  and  $\text{OH}^-$  rates.

## A. INTRODUCTION: What is the Experimental Situation?

Recent Ion Cyclotron Resonance (ICR) experiments<sup>1</sup> 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. Infrared laser radiation in the fluence range  $0.1$ - $3 \text{ Joules cm}^{-2}$  is used to vibrationally excite these anions which are in an ICR cell at  $\sim 10^{-6}$  torr. The ICR ion signal is found to decrease by an amount which depends upon the fluence (F) of the laser. The loss of ion signal has been attributed<sup>1,2</sup> to electron ejection caused by vibration-to-electronic (v-e) energy transfer within the isolated anion.

To compare the rates of IR photon absorption, intramolecular vibrational energy redistribution, and v-e energy transfer, it is useful to compute the average number  $\phi$  of IR photons per  $\text{cm}^2$  per sec which impinge on the ICR cell:  $\phi = 5.05 \times 10^{31} F (\bar{\lambda}\tau)^{-1}$ , with the fluence F in  $\text{Joules cm}^{-2}$ , the laser's pulse duration  $\tau$  in ns, and  $\bar{\lambda}$  the IR photon energy in  $\text{cm}^{-1}$ . Using  $\bar{\lambda} \sim 1000 \text{ cm}^{-1}$ ,  $\tau \sim 1000 \text{ ns}$ ,  $F \sim 0.1 \text{ J cm}^{-2}$ , which are in line with the experi-

mental conditions of ref. (1), gives  $\phi \sim 5 \times 10^{24}$  photons  $\text{cm}^{-2} \text{sec}^{-1}$ . An IR absorption cross-section of  $\sigma \sim 10^{-18} \text{cm}^2$  gives rise to an absorption rate of  $\phi\sigma \sim 5 \times 10^6$  photons  $\text{sec}^{-1}$ ; for  $F = 1 \text{ J cm}^{-2}$ ,  $\phi\sigma \sim 5 \times 10^7$ . Thus the ICR experiments produce sequential vibrational excitations spaced by  $\sim 20\text{-}200 \text{ ns}$ . This time between IR photon absorptions is much larger than the time  $0.1\text{-}0.001 \text{ ns}$  needed for intramolecular vibrational energy redistribution. Hence, it is likely that between IR photon absorptions, the energy is distributed among the vibrational-rotational modes of the anion even in the low-pressure ICR environment.

These IR absorption rates together with the laser pulse time ( $\sim 1000 \text{ ns}$ ) and the photon energy ( $\sim 1000 \text{ cm}^{-1}$ ) allow us to estimate that  $5\text{-}50$  photons (or  $0.6\text{-}6 \text{ eV}$  of energy) are absorbed by a typical anion prior to electron ejection. There can be more than enough energy in such anions to detach an electron (electron affinities of the anions studied range from  $0.3 \text{ eV}$  to  $\sim 2 \text{ eV}$ ) or to break chemical bonds. However, the rapid intramolecular energy redistribution makes it improbable that any one internal degree of freedom contains much greater than its equipartition "share" of this energy.

Statistical techniques such as RRKM theory<sup>3</sup> can be used to estimate how frequently any particular anion geometry is sampled given a total anion energy in the range  $\sim 0.6\text{-}6 \text{ eV}$ . If one were able both to identify those anion geometries near which  $v\text{-}e$  energy coupling is strong and to estimate the rate of  $v\text{-}e$  energy transfer, RRKM-like approaches might be used to test the  $v\text{-}e$  mechanism of refs. (1) and (2). Unfortunately, such a simulation of the ICR experiment is essentially impossible. Although we have some idea about the energy content of the anions studied in ref. (1), the experimental method (IR sequential photon absorption) simply does not permit one to precisely determine it. Moreover, for polyatomic anions it is a formidable task to search the anion and radical multidimensional potential energy surfaces for geometries where  $v\text{-}e$  coupling is large.

#### B. Theoretical Simulation for Limiting-Case Anions

## 1. Why $\text{LiH}^-$ and $\text{OH}^-$ ?

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 anions ( $\text{LiH}^-$  and  $\text{OH}^-$ ) which we view as limiting cases in the sense that v-e energy transfer should be very facile in  $\text{LiH}^-$  and very slow in  $\text{OH}^-$ . We chose to work on diatomic species to eliminate uncertainty about the energy content of the active vibrational mode.  $\text{LiH}^-$  was chosen because it has a small adiabatic detachment energy<sup>4</sup> ( $\sim 0.3$  eV) and because the energy and "size" of its  $3\sigma$  orbital (an sp hybrid orbital localized on the Li center directed away from the H center) are strongly affected by vibration of the Li-H bond. These facts make  $\text{LiH}^-$  an excellent candidate for rapid v-e energy transfer and rapid electron ejection.  $\text{OH}^-$  was chosen for study because it has a relatively large detachment energy<sup>5</sup> ( $\sim 1.8$  eV) and its active nonbonding  $\pi$  orbital is localized on the O center and is not strongly affected by motion of the O-H bond. Hence,  $\text{OH}^-$  is expected to yield small v-e coupling and slow electron ejection rates. Of course, the fact that  $\text{OH}^-$  and  $\text{LiH}^-$  contain 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 chemical treatment.

## 2. How Do We Evaluate the Ejection Rates?

An expression for the rate  $W(\text{sec}^{-1})$  of v-e electron ejection has been given<sup>2</sup>

$$W = \frac{2\pi}{\mu} \frac{\hbar^3}{2} \left| \langle x_{\nu}^0(\mathbf{R}) \int \phi_{\mathbf{k}}^*(\vec{r}, \mathbf{R}) \frac{d}{d\mathbf{R}} \phi_{-}(\vec{r}, \mathbf{R}) d\vec{r} \frac{d}{d\mathbf{R}} x_{\nu}^{-}(\mathbf{R}) \rangle \right|^2 \rho$$

in terms of the anion's active orbital  $\phi_{-}$  and vibrational wavefunctions  $x_{\nu}^{-}$ , the continuum orbital  $\phi_{\mathbf{k}}$  describing the ejected electron, and the neutral's vibrational wavefunctions  $x_{\nu}^0$ , and reduced mass  $\mu$ .  $\rho$  is the density of translational states of the free electron. The kinetic energy of the electron is determined by the difference between the anion ( $\epsilon_{\nu}^{-}$ ) and neutral ( $\epsilon_{\nu}^0$ ) vibrational energies:  $\frac{\hbar^2 k^2}{2m_e} = \epsilon_{\nu}^{-} - \epsilon_{\nu}^0$ .

Using highly accurate ab initio potential energy curves<sup>4</sup> ( $E^-(R)$ ,  $E^0(R)$ ) computed by Liu et al for  $\text{LiH}^-$  and  $\text{LiH}$ , we obtained the anion and neutral vibrational energies and wavefunctions (and hence  $\frac{d}{dR} \chi_v^-$ ). For  $\text{OH}^-$  and  $\text{OH}$ , spectroscopic data of Lineberger<sup>5</sup> and others<sup>6</sup> were used to determine the parameters of the Morse potentials.

The bound anion's electronic orbital  $\phi_-$  ( $3\sigma$  for  $\text{LiH}^-$ ,  $1\pi$  for  $\text{OH}^-$ ) was evaluated as a linear combination of Gaussian-type atomic orbitals  $\{g_j\}$ :  $\phi_-(\vec{r}, R) = \sum_j C_j(R) g_j(\vec{r}, R)$ . 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 LCAO-MO expansion coefficients  $\{C_j(R)\}$  were evaluated at numerous bond lengths ( $R$ ), using the Hartree-Fock self-consistent field procedure, and then least-squares fit to a polynomial in  $R$ . This fitting process allows  $\frac{d}{dR} C_j(R)$  and hence  $\frac{d}{dR} \phi_-$  to be straightforwardly evaluated. The continuum orbital  $\phi_k$  describing the ejected electron was approximated as a plane wave  $\exp(i\vec{k}\cdot\vec{r})$  orthogonalized to the occupied orbitals of the anion:  $\phi_k \sim \exp(i\vec{k}\cdot\vec{r}) - \sum_{j=\text{occupied}} \langle \phi_j | \exp(i\vec{k}\cdot\vec{r}) \rangle \phi_j$ . The wave-vector magnitude  $k$  is determined by the energy difference  $\epsilon_v^- - \epsilon_v^0$ . The deBroglie wavelength  $\lambda = \frac{2\pi}{k}$  of the ejected electron was found, for all of the  $\text{LiH}^-$  and  $\text{OH}^-$  transitions studied to be larger than 15 Å.

### 3. Results of Theoretical Simulation of Ejection Rates

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

One immediately notices that the state-to-state  $\text{LiH}^-$  detachment rates ( $2 \times 10^5 - 4 \times 10^9 \text{ sec}^{-1}$ ) are generally higher than those for  $\text{OH}^-$  ( $3 \times 10^1 - 6 \times 10^5 \text{ sec}^{-1}$ ). The sum of the rates of decay out of each anion level  $\epsilon_v^-$  into all accessible neutral levels  $\epsilon_v^0$ , determines the lifetimes of the  $\epsilon_v^-$  level. The decay lifetimes ( $10^{-9} - 10^{-10} \text{ sec}$  for  $\text{LiH}^-$  and  $10^{-5} - 10^{-6} \text{ sec}$

for  $\text{OH}^-$ ) are much longer than the anion's fundamental vibration period ( $2.829 \times 10^{-14}$  sec for  $\text{LiH}^-$  and  $9.033 \times 10^{-15}$  sec for  $\text{OH}^-$ ). Thus,  $\text{LiH}^-$  must vibrate at least 7000 times before an electron is ejected;  $\text{OH}^-$  requires at least  $10^8$  vibrations. The primary origin of this large difference in lifetimes lies in the fact that the  $\text{LiH}^-$   $3\sigma$  orbital has a much stronger R-dependence than does the  $1\pi$   $\text{OH}^-$  orbital (i.e.,  $\frac{d\phi^-}{dR}$  is larger for  $\text{LiH}^-$  than for  $\text{OH}^-$ ).

The long lifetimes predicted for these vibrationally hot anions have implications for experiments<sup>7</sup> 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.,  $\text{LiH}^- (v = 0) + h\nu \rightarrow \text{LiH}^- (v = 3)$ ) can also directly detach the electron via an electric dipole transition (e.g.  $\text{LiH}^- (v = 0) + h\nu \rightarrow \text{LiH} (v' = 0) + e$ ). Cross-sections ( $\sigma$ ) for the photodetachment (direct) process are typically  $\sim 10^{-17}$   $\text{cm}^2$ , and are relatively smoothly varying over energy ranges which are small with respect to vibrational spacings<sup>5</sup> of the neutral molecule. Fundamental infrared absorption cross-sections are  $\sim 10^{-18}$  -  $10^{-20}$   $\text{cm}^2$ , and overtone transitions usually have intensities which are ten times smaller for each overtone order n. 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 anions, the width of the resonance feature is not Heisenberg limited. Thus, it may be experimentally possible to detect the occurrence of the v-e process by looking for resonances in the photodetachment spectra of anions.

The data of Tables I and II also indicate that transitions which involve small energy changes are usually favored (e.g.,  $\text{LiH}^- (v = 7)$  decays at a much higher rate to  $v' = 3$   $\text{LiH}$  than to  $v' = 0, 1$ , or  $2$   $\text{LiH}$ ). To investigate the origins of these propensities, we performed a number of "model calculations" in which we artificially modified the overlaps between  $\chi_v^0$ ,

and  $\frac{d}{dR} x_v^-$ . By shifting the LiH or OH equilibrium bond length, we vary only  $x_v^0$ ;  $\epsilon_v^- - \epsilon_v^0$ , and  $\phi_k$  remain unchanged. We found that a 0.05 Å increase (decrease) in the LiH bond length gave rise to a ten-fold decrease (increase) in the various detachment rates. Similar changes in the OH bond length yielded similar changes in the OH<sup>-</sup> ejection rate. By shifting the relative equilibrium bond lengths ( $R_e$ ) of the anion and neutral, we move the vibrational functions  $x_v^0$ , and  $\frac{d}{dR} x_v^-$  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  $x_v^0$ ,  $\frac{d}{dR} x_v^-$  overlap are not independent since the local shapes of  $x_v^0$ , and  $x_v^-$  are determined by the local vibrational kinetic energies  $\epsilon_v^- - E^-(R)$  and  $\epsilon_v^0 - E^0(R)$ , respectively.

In summary, it seems that vibrational energy and momentum constraints, as embodied in the  $x_v^0$ ,  $\frac{d}{dR} x_v^-$  factors, are most important in determining the propensities. The electronic details dominate the absolute rate. 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  $\int \phi_k^* \frac{d}{dR} \phi_- d\vec{r}$  varies only weakly with  $\epsilon_v^- - \epsilon_v^0$ .

### C. 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 which should cover most molecular anions which have been experimentally studied to date, we carried out a fully ab initio study of LiH<sup>-</sup> and OH<sup>-</sup>. The lifetimes associated with electron loss of various

LiH<sup>-</sup> vibration levels ( $10^{-9}$  -  $10^{-6}$  sec) were found to be much shorter than those for OH<sup>-</sup> ( $10^{-5}$  -  $10^{-6}$  sec). The origin of this rate difference for these "limiting case" anions lies in the dependence of the anions' active orbital on bond length (R);  $\frac{d\phi}{dR}$  is much larger for the  $3\sigma$  orbital of LiH<sup>-</sup> than for the  $1\pi$  orbital of OH<sup>-</sup>. Even the shortest lived LiH<sup>-</sup> level has a Heisenberg width ( $\sim .1 \text{ cm}^{-1}$ ) 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 vibrational energy and momentum factors 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<sup>-</sup> and OH<sup>-</sup> 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<sub>2</sub>C<sup>-</sup>COH, in which the torsion and "puckering" of the H<sub>2</sub>C-group is treated as the single active vibration.

Table I. LiH<sup>-</sup> detachment rates ( $10^9 \text{ sec}^{-1}$ ) and

$v', v$	lifetimes ( $10^{-10}$ sec).							
	3	4	5	6	7	8	9	10
0	2.30	.34	.02	.0007	.002	.001	.01	.0002
1		4.83	1.61	.20	.01	.006	.007	.004
2				4.04	.80	.08	.01	.02
3					3.34	1.96	.34	.04
4							2.82	.84
Life-times	4.35	1.94	6.12	2.36	2.41	4.87	3.15	11.0

Table II. OH<sup>-</sup> detachment rates (10<sup>5</sup> sec<sup>-1</sup>) and lifetimes (10<sup>-6</sup> sec)

v', v	5	6	7	8	9	10	11
0	.65	1.36	.55	.15	.03	.005	.0003
1			3.97	2.84	1.12	.35	.09
2				1.79	5.96	3.67	1.59
3						3.41	5.87
Life-times	15.4	7.35	2.21	2.09	1.41	1.35	1.30

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