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Vibrational Excitation of Polar Molecules by Slow Electrons: HCl†

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Shape resonances cannot explain the strong vibrational excitation observed in the impact of electrons on polar molecules at threshold, because an important *s*-wave component in the wave function inhibits trapping. We explain the main features observed in HCl by invoking the concept of a virtual state to account for an enhancement of the wave function of a slow departing electron.

Very large cross sections ($\sim 10^{-15}$ cm^2) have recently been observed for electrons exciting vibrations in polar molecules near the lowest vibrational threshold.[1,2] Within 0.5 eV of the thresholds, the observed cross sections are larger by factors of 10–100 than estimates with Born's approximation.[3]

Up to now, the dominant mechanism for vibrational excitation of molecules by electron impact at energies below 10 eV has been thought to be temporary trapping of the incoming electron in a compound state at a shape resonance.[4] However, the shape resonance mechanism cannot explain the large vibrational excitation cross sections observed at thresholds[1,2] because in this case there can be no trapping within a centrifugal potential barrier, as at an electron shape resonance in a molecule. Such trapping is impossible because the angular distributions suggest a strong *s* wave,[1,2] through which an electron can escape without having to tunnel through a centrifugal barrier.

In HCl, the total cross section near the threshold for the excitation $v=0 \rightarrow v=1$ (where v is the vibrational quantum number) shows a peak about 0.2 eV wide[1]; at the peak, the cross section (integrated over scattering angles) reaches 2×10^{-15} cm^2 (see Fig. 1). At the next threshold, there is a similar but smaller peak for $v=0 \rightarrow v=2$, but none for $v=0 \rightarrow v=1$.

We have considered how the threshold peaks might arise from an enhancement of the wave funtion of a very slow departing electron at the molecule. Consider first a fictitious molecule which is roughly spherically symmetric, and whose potential vanishes outside a radius r_0 of molecular dimensions. Let the final state $\psi_f(r,k)$ be an *s* wave, normalized so that its incoming part as $r \rightarrow \infty$ is $(-)\exp[-i(kr+\delta_f)]/(2ikr)$, where r is the distance of the electron from the mass center, k is the wave number, and δ_f is the phase shift. ψ_f is defined for an electron in the potential from a molecule with nuclei frozen at their equilibrium positions. One finds $\psi_f(r_0, k=0) = 1 - a/r_0$, where a is the scattering length.[5] The corresponding amplitude for the free incident wave is 1, so that strong enhancement of the amplitude [i.e., $|\psi_f(r_0,$

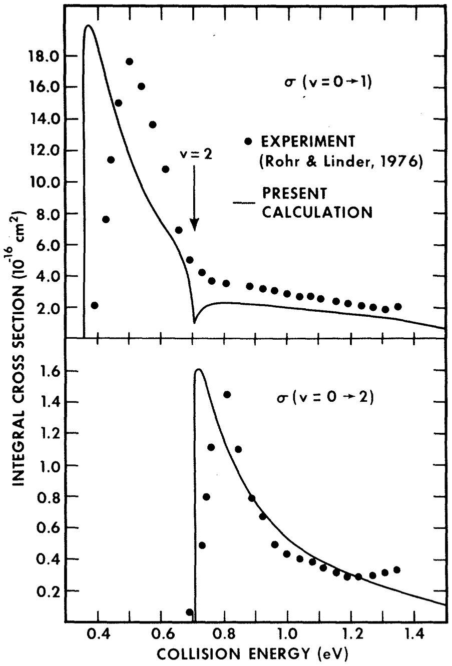

FIG. 1. Vibrational exciation cross sections for electrons on HCl. The experimental resolution is "in the range of 60 meV"; the accuracy of the experimental cross sections is "estimated to about 50% for the threshold peak and to about 20–30% for the rest of the curves." The theoretical curve was calculated for three channels; very similar results were obtained for five channels.

$k=0)|\gg 1]$ exists if $|a|\gg r_0$. If $a>0$, there is a bound state, whereas if $a<0$, one speaks of a "virtual state".[5]

In the case of the polar molecule, we use r_0 to distinguish between the molecular core in $r<r_0$, and the tail of the dipole potential in $r>r_0$. We show later that when $r>r_0$, one can still decompose the final-state wave function into angular modes, of which a single one dominates at low energies. That special mode is concentrated slightly on the positive side of the molecule. We shall show that it can lead to a strong enhancement of the wave function at the molecule at low energy, very much like the virtual state in spherical symmetry; we shall also show, in Fig. 1, that it can account for the observed threshold peaks in the cross sections.

Consider an electron with spherical coordinates (r,θ,φ) near a polar diatomic molecule whose charge center is at the origin, and whose axis is fixed. (We return later to the problem of rotation.) Draw a sphere of radius r_0, such that the electron sees a dipole potential

$$V(\vec{r}) = -D\cos\theta/r^2 \text{ for } r>r_0. \tag{1}$$

D is the dipole moment of the molecule; $\theta=0$ corresponds to points on the axis on the positive side of the molecule. We use atomic units throughout, so that $\hbar$, the mass of the electron, and the charge of the electron are all equal to 1. The radius r_0 is to be the smallest for which the potential (1) is a good approximation when $r>r_0$. We shall take vibration of the molecule into account by writing

$$D = q_0R_0 + q_1Q, \tag{2}$$

where R_0 is the equilibrium separation of the nuclei in the neutral target, and Q is the coordinate which describes nuclear vibration along the axis; moreover, $q_0 \equiv D(Q=0)/R_0$ and $q_1=(\partial D/\partial Q)_{Q=0}$. We used the values $q_0=q_1=0.176$, corresponding to the observed $R_0=2.408a_0$. The linear approximation in (2) is justified for low vibrational states, where Q is of order $M^{-1/4}$; here M is the nuclear mass, so that $M^{-1/4}\approx 0.1$.

The Hamiltonian is $H=H_v+K+V+L^2/2r^2$, where H_v describes the vibration of the molecule, K is the radial kinetic energy of the extra electron, L the orbital angular momentum of the electron, and V the potential of interaction between the extra electron and the molecule. In the region $r>r_0$ it is convenient to introduce the angular functions $\Omega_n(\hat{r})$ defined by

$$[\tfrac{1}{2}L^2 - q_0R_0\cos\theta + \tfrac{1}{2}A_n]\,\Omega_n(\hat{r}) = 0, \tag{3}$$

where the eigenvalues A_n are chosen so as to make Ω_n continuous with continuous first derivatives over the unit sphere. We normalize the functions Ω_n so that $\int \sin\theta d\theta d\varphi_n \Omega_n{}^*\Omega_m = 1$ if $n=m$, and zero otherwise. The spherical polar angles (θ,φ) correspond to the direction of the unit vectors $\hat{r}$ appearing in Ω_n and Ω_m.

In the region $r>r_0$ we make the approximation of retaining only the function Ω_0 belonging to the lowest eigenvalue A_0 in (3). Thus, we approximate the wave function for $r>r_0$ by $\Phi(\vec{r},Q)=\Psi_0(r,Q)\Omega_0(\hat{r})$. The function Ω_0 has no nodes in either θ or φ; it peaks in the attractive minimum of the potential (1). This mode gives rise to the strongest attractive potential $-A_0/2r^2$ in the radial equation for the extra electron. We find $A_0=0.1197$ for $D=1.1$ D, as in HCl. The Schrödinger equation at energy E becomes, when $r>r_0$,

$$\left(K - \frac{A_0}{2r^2} - \frac{CQ}{r^2} + H_v - E\right)\Psi_0(r,Q) = 0, \tag{4}$$

where

$$C \equiv q_1 \int \sin\theta d\theta d\varphi |\Omega_0(\hat{r})|^2 \cos\theta.$$

The next two A_n values, which we neglect, are $A_1 = -1.963$, $A_2 = -2.070$, for $D = 1.1$ D for HCl; they both give rise to such strongly repulsive potentials that the radial wave function in the corresponding angular mode is negligible at the molecule at energies below 1 eV. Physically, the combination of the single angular mode Ω_0 and the attractive potential $-A_0/2r^2$ in Eq. (4) represents a slight channeling of the projectile toward the positive end of the molecule.

Within the sphere $r = r_0$ the extra electron sees a potential considerably more complicated than the dipole potential in Eq. (1). To avoid calculating in this region, we introduce the logarithmic derivative of $\Psi_0(r,Q)$ at $r = r_0$:

$$[\partial\Psi_0(r, Q)/\partial r]_{r=r_0} = f(Q)\Psi_0(r_0, Q). \tag{5}$$

The function $f(Q)$ is determined by the wave function in the region $r < r_0$ where the potential is strong (~1 a.u.), so that one may suppose the wave function to follow the nuclei adiabatically. Hence f is determined by the instantaneous position Q of the nuclei. Moreover, if the impinging energy is small ($\lesssim$1–2 eV) compared with the strength of the internal potential, one may ignore the variation of f with energy. Since the vibrational amplitudes of the nuclei are small in low vibrational states ($\sim M^{-1/4} \approx 0.1$) in comparison with the Bohr radius, we expand f to first order in Q, and write

$$f(Q) = f_0 + f_1 Q. \tag{6}$$

We took $r_0 = 2a_0$, so that 90% of the charge on H is in the region $r < r_0$.

The parameters f_0 and f_1 may be adjusted to fit experiments. Estimates may be made in the following way, with two extreme models for the wave function within $2a_0$ of the charge center. In one model, the incoming electron sees the configuration (Cl)(H); in the second, it sees $(\mathrm{Cl}^-)(\mathrm{H}^+)$. (In the neutral HCl molecule, the dipole moment corresponds to 0.82 of an electron near the proton.) In the first case, with the configuration (Cl)(H), the wave function near the proton should look like H^-; from published calculations,[6] one finds $f_0 = -0.28$, while $f_1 = 0$ if the perturbation from the neutral (Cl) is neglected. In the second model, with the configuration $(\mathrm{Cl}^-)(\mathrm{H}^+)$, we have constructed a superposition of s and p waves near the proton which interfere constructively outside the positive end of the molecule; the energy was zero, and a constant potential was included equal to the potential from the Cl^- at the proton. We find $f_0 = -0.75$, $f_1 = -0.25$.

The approximation of the fixed axis is implicit in the Schrödinger equation (4). If $\vec{\omega}_{\mathrm{rot}}$ is the angular velocity of the nuclei, and I the moment of inertia, the approximation requires that the Coriolis term $\vec{\omega}_{\mathrm{rot}} \cdot \vec{\mathrm{L}}$ and the differences of the eigenvalues of the rotational kinetic energy $\frac{1}{2}I\omega_{\mathrm{rot}}^2$ should be small compared with the potential $A_0/2r^2$ in (4). Estimates at room temperature suggest that this condition is satisfied if $r \lesssim r_c = 50a_0$ ($a_0 = 0.52 \times 10^{-8}$ cm). The transit time of an electron of energy 0.05 eV from $r = r_c$ to $r = r_0$, and back out again to $r = r_c$ is less than $\frac{1}{10}$ of the period of nuclear rotation. Therefore, we have used the fixed-axis model for $r < r_c$. At $r = r_c$, one has $A_0/2r_c^2 = 0.5 \times 10^{-3}$ eV; therefore, we have ignored the electron-molecule interaction in the region $r > r_c$.

We have solved Eqs. (4) and (5) numerically for $r_0 < r < r_c$ by expanding

$$\Psi_0(r,Q) = \sum_{v=0}^{v_{\max}} \chi_v(Q) \frac{\Psi_{0v}(r)}{r}, \tag{7}$$

where $\chi_v(Q)$ is the vth vibrational state of the molecule. We took $v_{\max} = 2$ or 4. The functions $\Psi_{0v}(r)$ satisfy equations obtained by projecting (4) onto the different vibrational states $\chi_v(Q)$; they may be split up into incoming waves $\Psi_{0v}^{(-)}(r)$ and outgoing waves $\Psi_{0v}^{(+)}(r)$, such that $\Psi_{0v} = \Psi_{0v}^{(-)} + \Psi_{0v}^{(+)}$. The amplitudes $\Psi_{0v}^{(-)}(r_c)$ at $r = r_c$ were taken to be

$$\frac{\Psi_{0v}^{(-)}(r_c)}{r_c} = \delta_{0v} \int d\hat{r}\,\Omega_0(\theta,\varphi)[\exp(i\vec{\mathrm{k}}_0 \cdot \vec{\mathrm{r}}]_{\mathrm{in},\,r=r_c}, \tag{8}$$

where $[\exp(i\vec{\mathrm{k}} \cdot \vec{\mathrm{r}})]_{\mathrm{in},\,r=r_c}$ is the incoming wave part of the incident plane wave at $r = r_c$, and where $\delta_{0v} = 1$ if $v = 0$, and zero otherwise. The amplitudes $\Psi_{0v}^{(+)}$ were then determined from (5) and (6) at $r = r_0$. The outgoing waves in $r > r_c$ were taken for free electrons near a neutral molecule with a fixed axis. Their amplitudes in the different vibrational channels were set equal to $\Psi_{0v}^{(+)}(r_c)\Omega_0$ at $r = r_c$. In joining the wave function in the region $r < r_c$ to incoming and outgoing waves at $r = r_c$, we have taken only the s-wave component of Ω_0 into account because $|\int d\hat{r}\, Y_{00}^*(\hat{r} \cdot \hat{R})\Omega_0(\hat{r},\hat{R})|^2 = 0.945$, which is close to unity, for the dipole moment of HCl. The total cross section for the transition $v = 0 \rightarrow v = v_f$ becomes

$$\sigma_T(v = 0 \rightarrow v = v_f) = 0.945(k_f/k_0)|\Psi_{0v}^{(+)}(r_c)|^2, \tag{9}$$

where k_0 is the incoming and k_f the outgoing momentum. It has to be emphasized that in the re-

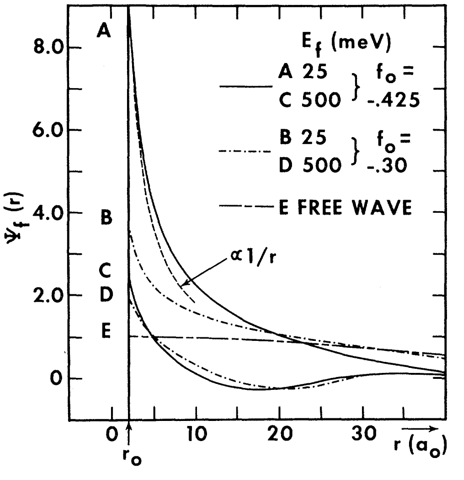

FIG. 2. Enhancement of the final state at the molecule: the final-state wave function $\psi_f(r)$. The normalization is $\psi_f(r) \to \sin(k_f r + \delta_f)/(k_f r)$ as $r \to \infty$; the corresponding free-electron wave function $\sin(k_f r)/(k_f r)$ is also shown for final energy $E_f = 25$ meV. Note that $|\psi_f(r_0)| \gg |$ free wave at $r = r_0|$.

gion $r < r_c$, a slight concentration of Ω_0 near the positive end of the molecule takes account of the channeling of the impinging electron toward the H atom.

The excitation cross sections for the first two vibrational levels have been calculated by treating f_0 and f_1 as adjustable parameters. The best fit to the total cross section, integrated over all final directions $\hat{k}_f$, is shown in Fig. 1; it corresponds to $f_0 = -0.425$ and $f_1 = -0.51$ for $v_{\max} = 2$. For five channels ($v_{\max} = 4$), very similar results are obtained for $f_0 = -0.545$ and $f_1 = -0.51$. The values of the parameters which give the best fit are of the order estimated after Eq. (6). The values of f_0 and f_1 were chosen mainly with regard to the shape of the cross-section curves, and the ratio of the observed peaks at threshold. The calculation reproduces the main features of the observations, both in energy dependence and in order of magnitude. The observed near-spherical symmetry of the angular distribution is consistent with the large overlap of Ω_0 and Y_{00} for the dipole moment of HCl.

The origin of the large cross sections at threshold is suggested by Fig. 2, which shows the wave function $\psi_f(r)$ in the final state. This function is a solution of (4), (5), and (6), with $C = f_1 = 0$ and $E - H_v = \frac{1}{2}k_f^2$. The normalization is such that $\psi_f(r) \to \sin(k_f r + \delta_f)/(k_f r)$ as $r \to \infty$, where δ_f is the phase shift. The amplitude $\psi_f(r_0)$ at the molecule is seen to be greatly enhanced over the free-electron wave function $\sin(k_f r)/(k_f r)$, particularly if ψ_f belongs to the value $f_0 = -0.425$ which gives the best fit in Fig. 1.

Note that the potential $-A_0/2r^2$ in Eq. (4) does not possess a barrier. Note also that the dashed curve in Fig. 2 shows that $\psi_f(r) \propto 1/r$ in the neighborhood of the molecule. By contrast, a shape resonance would be associated with a potential barrier, within which the wave function falls off much more rapidly than $1/r$. The function ψ_f does not behave like that; instead, it resembles a virtual s-state wave function in a spherically symmetric potential well of finite range without a barrier; this virtual state too varies as $1/r$ outside the potential well. We therefore interpret the observed threshold peaks as being due to a virtual state.

With the values $f_0 = -0.425$, which give the best fit to the experiments, one has $[(r\psi_f)^{-1} r\partial(r\psi_f)/\partial r]_{r_0} \ll 1$. Therefore, the molecular core alone would possess a virtual state, which is then somewhat modified by the tail of the dipole potential. (We are indebted to Charles Clark for this remark.)

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