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Ab initio study of vibrational excitation of HF by low-energy electrons

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Fixed-nuclei, static-exchange calculations have been performed to study the vibrational-rotational excitation of HF by electrons from threshold to 5 eV. Our calculated, R-dependent K-matrix elements in $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ symmetry are combined with exact point-dipole and laboratory-frame first-Born-approximation results for higher symmetries to obtain converged, integrated cross sections. The calculations show strong threshold peaks which are related to the dependence of the $^2\Sigma^+$ K-matrix elements on internuclear distance at small scattering energies.

The observations by Rohr and Linder[1,2] of sharp resonance peaks in the cross sections for vibrational excitation of the hydrogen halides by electron impact have triggered a considerable amount of theoretical work[3] aimed at interpreting these structures. The bulk of this work has been of a qualitative nature, based on simple models of the electron-molecule interaction potential. The most ambitious computations to date have been those of Rudge,[4] who performed close coupling calculations in the laboratory frame for rotational-vibrational excitation of HF by electrons in the energy range 0.46–2.0 eV. Rudge used a model interaction potential, based on approximating the first three multipole terms in the $e^- + \mathrm{HF}$ static potential. Furthermore, exchange and polarization effects were not included. Rudge's calculations[4] succeeded in reproducing the main features observed in the experimental vibrational excitation cross sections[2]; however, his results showed that the magnitude and width of the threshold peaks, as well as the magnitude of the cross sections away from threshold, were quite sensitive to the short-range part of the potential, which in turn was determined by a single adjustable parameter.

The purpose of this Communication is to report the results of *ab initio* calculations of simultaneous rotational and vibrational excitation cross sections for HF. To evaluate these cross sections, we performed fixed-nuclei calculations of the K matrix in $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ symmetries for five different internuclear separations in the 0–5-eV energy range. These calculations were performed using the static-exchange approximation with a Hartree-Fock target wave function, and were based on a single-center formulation of the collision problem.[5] For higher symmetries, we used exact point-dipole[6] and laboratory-frame first-Born K-matrix elements.[7]

The coupled, single-center, static-exchange equations were solved numerically using the recently developed separable-exchange technique of Rescigno and Orel.[8,9] This technique is based on the representation of the exchange potential by a sum of separable terms and uses an integral equations algorithm to propagate the solutions outwardly in a stable,[9] noniterative fashion. The static potentials were obtained from self-consistent-field (SCF) wave functions for HF calculated using a double ζ level plus polarization basis of contracted Gaussian functions.[10] This basis was augmented with additional tight and diffuse basis functions to form the separable representation of the exchange potentials. Terms up to $l = 10$ were retained in the expansion of the occupied and scattering orbitals, and up to $\lambda = 20$ in the expansion of the static potential. Piecewise trapezoidal quadrature meshes were used in solving the coupled equations. Because of the long-range nature of the electron-dipole interaction potential, the integrations had to be carried out to large distances.

Although the eigenphase sums were found to converge rather rapidly, the individual K-matrix elements could be quite sensitive to a premature cutoff of the numerical integration. We therefore carried the integrations to a point where the ratio of the static potential to the collision energy was less than 10^{-4}, e.g., up to 5100 a.u. for a value of $k = 0.02$. This insured that the computed $K_{l,l\pm 1}$ matrix elements went over properly to the correct, energy-independent, Born limit for high l values.

Figure 1 displays our calculated $^2\Sigma^+$ eigenphase sums. It is particularly noteworthy that the rise in the eigenphase sum with decreasing energy becomes progressively sharper with increasing internuclear distance (increasing dipole moment). This low-energy behavior ($k = 0.01$ a.u. was the smallest value of k considered) is entirely consistent with the behavior expected[11] for a stationary supercritical dipole and will be seen to give rise to structure in the vibrational excitation cross sections near threshold. It should be noted that for all five R values, the calculated HF dipole moment exceeds the critical value required to bind a σ electron (total symmetry $^2\Sigma^+$). This is not the case for higher symmetries. Indeed, our computed $^2\Pi$ and $^2\Delta$ eigenphase sums (not shown) were found to display no anomalous behavior and to limit smoothly to the correct, energy-independent, dipole limits[6] as $k \rightarrow 0$.

It is well known[5,7,12] that a fixed-nuclei treatment of electron-polar molecule scattering leads to divergent integrated cross sections, owing to the slow ($1/l$) falloff of the K-matrix elements for large l and the consequent logarithmic divergence of the partial-wave series. This is an essential property of the dipole potential. A remedy[13,14] for this apparent dilemma, and the one we have adopted, is to begin with a simple approximation to the integrated cross section in a complete representation that accounts for rotational motion of the molecule and to use the fixed-nuclei approximation to evaluate the correction to

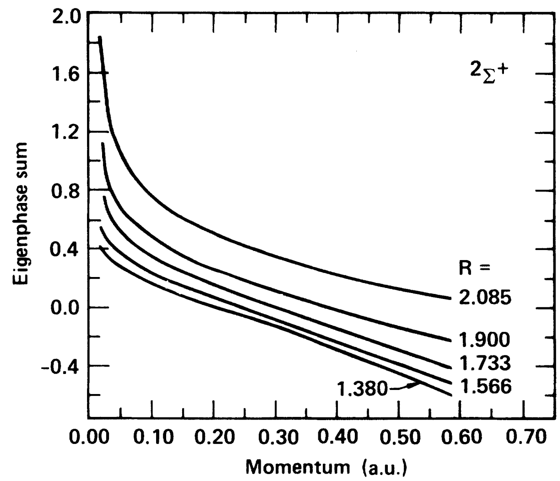

FIG. 1. Fixed-nuclei $^2\Sigma^+$ eigenphase sums for $e^- + \mathrm{HF}$ calculated in the static-exchange approximation for five internuclear separations.

this zeroth-order result. Choosing the first-Born approximation for a rotating point dipole as the starting point,[13,14] we write the integral cross section for a particular rotational-vibrational transition as

$$\sigma_{vj\rightarrow v'j'} = \sigma^{\mathrm{Born}}_{vj\rightarrow v'j'} + \Delta\sigma_{vj\rightarrow v'j'} \ , \tag{1}$$

$$\sigma^{\mathrm{Born}}_{vj\rightarrow v'j'} = \frac{8\pi}{3k_{vj}^2} |D_{vv'}|^2 \frac{j_>}{2j+1} \ln \left| \frac{k_{vj} + k_{v'j'}}{k_{vj} - k_{v'j'}} \right| \ , \tag{2}$$

where $D_{vv'}$ is a matrix element of the R-dependent dipole moment between initial and final vibrational wave functions and $k_{vj}(k_{v'j'})$ denotes the initial (final) electron momentum. $\Delta\sigma_{vj\rightarrow v'j'}$, the difference between the exact cross section and the laboratory-frame first-Born result, is rapidly convergent in l at low energy and was hence evaluated in the adiabatic-nuclei approximation:

$$\Delta\sigma_{vj\rightarrow v'j'} = \frac{\pi}{(2j+1)k_{vj}^2} \sum_{J=0}^{\infty} \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} (2J+1)(|T^J_{lj,l'j'}|^2 - |T^{J(\mathrm{Born})}_{lj,l'j'}|^2) \ . \tag{3}$$

Both $T^J_{jj'}$ and $T^{J(\mathrm{Born})}_{jj'}$ were computed from body-frame T-matrix elements using the frame transformation[15]

$$T^J_{lj,l'j'} = (-1)^{l+l'} \sum_{m=-J}^{J} (Jl-mm|j0)(Jl'-mm|j'0) T^m_{ll'} \ , \tag{4}$$

where

$$T^m_{ll'} = \int \phi_v(R) T^m_{ll'}(R) \phi_{v'}(R) dR \ , \tag{5}$$

and

$$T^m_{ll'}(R) = \left[\frac{2\underline{K}^m(R)}{1 - i\underline{K}^m(R)} \right]_{ll'} \tag{6}$$

and $(Jl-mm|j0)$ is a Clebsch-Gordan coefficient.

For a fixed collision energy, $T^m_{ll'}(R)$ rapidly approaches the first-Born limit for a point dipole:

$$T^m_{ll'}(R) \underset{l\rightarrow\infty}{\longrightarrow} T^{m(\mathrm{Born})}_{ll'}(R) = -\delta_{l',l\pm 1} \frac{4D(R)}{2l_>} \left(\frac{(l_> + m)(l_> - m)}{(2l_> - 1)(2l_> + 1)} \right)^{1/2} \ . \tag{7}$$

Consequently, the sums in Eq. (3) converge very rapidly. We found it adequate to retain terms through $J=4$ (and consequently $|m|=4$) in evaluating $\Delta\sigma_{vj\to v'j'}$. To compute $T^{m}_{ll'}$, we used our fixed-nuclei, static-exchange K-matrix elements for $|m|=0, 1, 2$ and the exact K matrices appropriate for a point-dipole potential[6] for $|m|=3, 4$. The integrations over R required in Eq. (5) were performed using the five-point Gauss-Hermite quadrature and Morse oscillator wave functions for $\phi_v(R)$, with parameters corresponding to experimental spectroscopic values.[16]

The fixed-nuclei, electronic scattering amplitude $T^{m}_{ll'}(R)$ is on the energy shell and is a function of a single energy parameter, k^2. It is not possible to rigorously identify this parameter with either k^2_{vj} or $k^2_{v'j'}$, and a precise definition is required very close to threshold. We have followed Norcross and Padial's suggestion[14] of choosing $k^2=k_{vj}k_{v'j'}$ as an approximation to Nesbet's energy-modified adiabatic approximation.[17] This choice has the obvious advantage of associating thresholds in the physical cross sections with threshold in the body-frame calculations.

Figure 2 displays our computed cross sections for exciting the first four rotational levels of the $v=1$ vibrational state from the $j=0$, $v=0$ level of HF. The $j=0\to 1$ cross section is seen to rise very sharply at threshold. The secondary, broad peak in this cross section above 1 eV arises from the contribution of high partial waves which are included in the first-Born approximation. The $j=0\to 0$ rotational cross section dominates at energies below 2 eV, although it does not rise as sharply as the $j=0\to 1$ cross section.

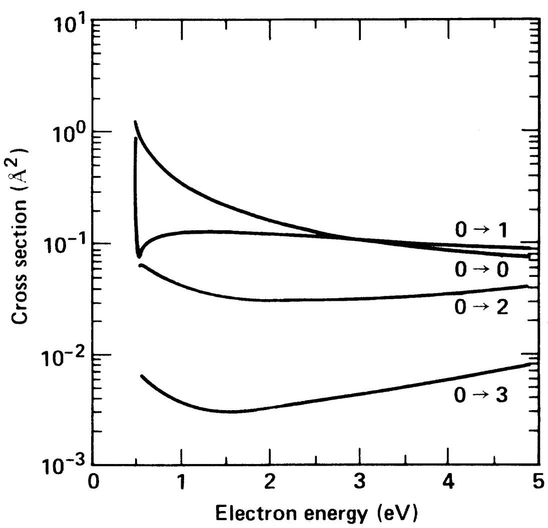

FIG. 2. The calculated $v=0\to 1$ rotational-vibrational excitation cross sections for $e^-+\mathrm{HF}$. The individual curves correspond to cross sections for specific rotational transitions.

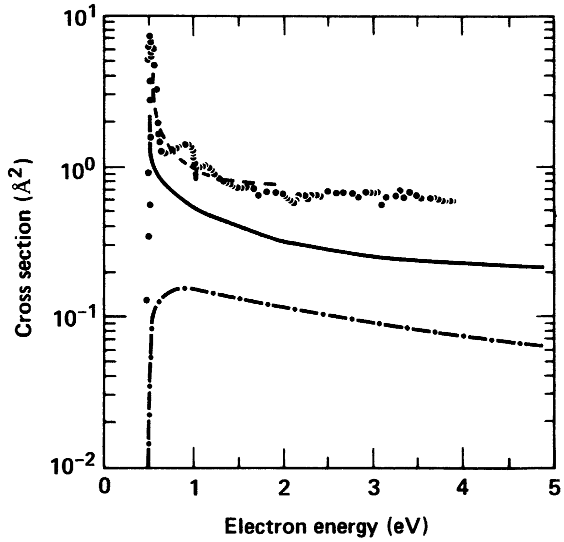

FIG. 3. Cross sections (rotationally summed) for excitation of the $v=1$ state of HF by electron impact: solid curve (——), present results; dashed curve (– – –), theoretical results of Rudge (Ref. 4); dashed-dot curve (–·–·), dipole-Born approximation; dots (· · · ·), experimental results of Rohr and Linder (Ref. 2).

Figures 3 and 4 compare our $v=0\to 1$ and $v=0\to 2$ cross sections, summed over the final rotational levels, with those of Rudge[4] and the experimental results of Rohr and Linder.[2] The dipole-Born [Eq. (2)] results are also shown for comparison. Our cross sections display the same energy dependence as the experimental results[2] but are approximately a factor of 2 smaller in magnitude for $E>1.2$ eV. How-

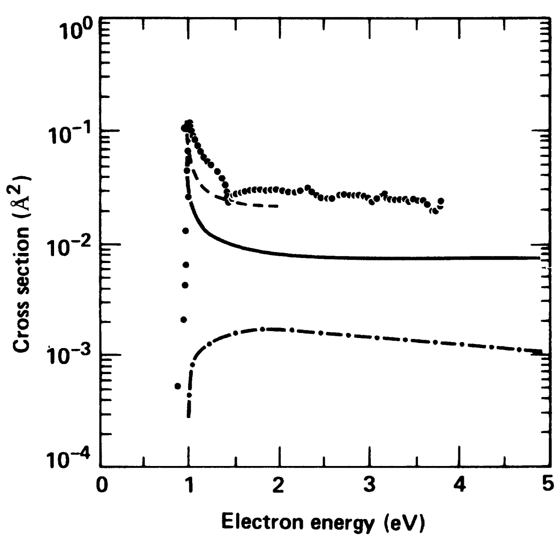

FIG. 4. As in Fig. 3, for $v=0\to 2$.

ever, Rohr and Linder[2] report a factor-of-2 uncertainty in the absolute magnitude of their angle-integrated data, which was in turn normalized to their HCl measurements.[1,2] Moreover, a comparison of their differential elastic scattering cross sections with independent theoretical calculations[18,19] suggests that the HCl data are a factor of 2 too large. If this were true, then our *ab initio* results would be quite close to Rohr and Linder's integrated cross sections[2] away from threshold.

At energies above 0.6 eV, Rudge's theoretical results[4] are consistent with our calculations. Rudge finds that his calculated cross sections decrease with decreasing values of Q', the derivative of the HF quadrupole moment. We have plotted his results obtained with $Q' = 2.10$ a.u. In contrast, our *ab initio* calculations give $Q' \approx 1.6$ a.u. at R_e. Judging from the trend of Rudge's results, using $Q' = 1.6$ a.u. in his model would produce cross sections close to our results at energies away from threshold. The threshold features in Rudge's cross sections, however, appear to become less pronounced as Q' decreases and they are evidently more sensitive to the detailed features of the short-range potential, including exchange.

There are several conclusions one can draw from the present calculations. For energies at least 0.1 eV above threshold, the adiabatic-nuclei, static-exchange approximation[5] evidently gives a reasonable accounting of the magnitude and the energy dependence of the observed vibrational excitation cross sections for HF. It also shows that in the adiabatic-nuclei approximation, the threshold peaks are related to the strong dependence of the $^2\Sigma^+$ K-matrix elements on internuclear distance at small scattering energies. Furthermore, our calculations show no evidence of a $^2\Sigma^+$ shape resonance below 3 eV. In the theoretical model developed by Domcke and Cederbaum,[11] the threshold peaks are attributed to the interaction between a broad shape resonance and the background scattering continuum of a nonrotating, fixed dipole. Our results indicate that for the case of HF, sharp threshold peaks can be obtained from adiabatic-nuclei calculations without invoking such a resonance model. Nevertheless, we cannot rule out the possibility that these features are due in part to the use of the adiabatic-nuclei approximation which breaks down close to thresholds. Nonadiabatic effects, which require a dynamical treatment of the nuclear motion, will have to be included to determine the magnitude and the width of the threshold peaks.

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