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Ro-vibrational excitation of HCl by electron impact

N. T. Padial and D. W. Norcross*

*Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards,
Boulder, Colorado 80309*

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Ab initio calculations of cross sections for simultaneous rotational and vibrational excitation of HCl by low-energy electrons have been made in the multipole-extracted adiabatic-nuclei approximation. These calculations employed a free-electron-gas model of the exchange interaction, and represent the first application of a new parameter-free model of the correlation-polarization interaction to vibrational excitation. The cross sections increase by an order of magnitude with the inclusion of this interaction, which is much more important for vibrationally inelastic than elastic collisions.

In 1975, Rohr and Linder[1] observed remarkable resonance structure in cross sections for vibrational excitation of HCl by electron impact. Similar features were later observed[1,2] in other polar and nonpolar molecules. Although these results stimulated a large amount of theoretical work, most of it based on phenomenological models of the electron-molecule interaction potential, the interpretation of the experimental results remains controversial.[3] This is a preliminary report of the first *ab initio* calculations for HCl, the continuation of an earlier study[4] of vibrationally elastic scattering. This study has several goals: to help understand the source of the observed resonance structure and the curious isotropy of the differential cross sections; to explore the sensitivity to various models of the exchange and polarization interactions; and to provide a more accurate reference for absolute normalization of the measured results. All parameters governing precision and convergence were chosen to achieve results numerically accurate to better than 1%.

The scattering calculations were carried out using a single-center, integral-equations formulation[5] of the close-coupling approximation. The equations were solved in the molecular body-fixed (BF) coordinate frame in the fixed-nuclei approximation for seven values of R (internuclear distance) from $1.8a_0$ to $3.2a_0$. The static interaction potential was obtained by integrating[6] the electrostatic interaction over the ground electronic state of HCl, which was defined by a near Hartree-Fock wave function.[7] Exchange (except as noted below) was treated using a local, energy dependent, free-electron-gas (FEG) approximation,[8] which is a function of the molecular charge density $\rho(R, \vec{r})$ and the ionization potential of HCl (computed for each value of R using Koopman's theorem). The number of moments required in the Legendre expansions of the nuclear (35–39), electronic (17–19), and exchange (17–19) potentials were found to increase with R. This model of the interaction potential is denoted SE, for static exchange.

Calculations were also performed with this model augmented by a new parameter-free model of the correlation-polarization (COP) potential,[9] which obviates the need for

any semiempirical adjustment or tuning as in the earlier[4] work. This also has a simple dependence on $\rho(R, \vec{r})$, and on the molecular polarizabilities.[10] Only the monopole and quadrupole terms (those that couple to the isotropic and quadrupole polarizabilities) were retained in the expansion of the correlation potential, other moments being negligible compared to the SE potential. This model of the interaction potential is denoted SECOP.

The scattering equations were solved for five collision symmetries from Σ to Γ. The maximum order of channel angular momentum l_c (17–29) in the partial-wave expansion of the continuum wave functions required for convergence of the scattering calculations was also found to be an increasing function of R. Orthogonality of the scattering wave function to all bound orbitals of like symmetry was imposed throughout. When required, these orbitals were expanded in a single-center representation over all scattering channels. The scattering equations were integrated to a radius of $10l_c/k$, where k^2 is the BF frame collision energy in rydbergs, before reactance matrices were extracted by matching to plane waves.

Differential cross sections in the laboratory-fixed (LF) frame were obtained using the multipole-extracted adiabatic-nuclei (MEAN) approximation:[11]

$$\frac{d\sigma}{d\Omega}(vj\text{-}v'j') = \frac{d\sigma^{\text{FBA}}}{d\Omega}(vj\text{-}v'j') + \Delta\frac{d\sigma}{d\Omega}(vj\text{-}v'j') \ , \quad (1)$$

where

$$\Delta\frac{d\sigma}{d\Omega}(vj\text{-}v'j') = \frac{k_{v'j'}}{4k_{vj}}\sum_{l_t}C(jl_tj';00)^2\frac{1}{k^2}\sum_{\lambda}(B_{\lambda,l_t} - B_{\lambda,l_t}^{\text{FBA}}) \ . \quad (2)$$

The index l_t denotes the angular momentum exchanged during the collision, and $C(\dots)$ is a Clebsch-Gordan coefficient. The first term in (1) is a closed-form expression for a particular cross section in the LF frame in the first-Born approximation (FBA). The second term in (2) is the

partial-wave representation of the same cross section in the AN approximation. These two terms are used only for $l_t = 1$ and 2, and involve the molecular dipole moment D, and quadrupole moment Q and polarizability α_2, respectively. This ensures most rapid convergence of the sum over λ in (2), and is essential for $l_t = 1$ since in this case the two sums individually diverge. Six terms (0–5) were retained in the sum over l_t in (2).

The LF frame momenta k_{vj} and $k_{v'j'}$ of the electron are related by

$$k_{vj}^2 - k_{v'j'}^2 = B_{v'}j'(j'+1) - B_v j(j+1) + E_{vv'} , \quad (3)$$

where B_v is the rotational constant of HCl in vibrational state v, and $E_{vv'}$ is the energy difference of the initial and final vibrational states (we used measured values of these quantities[12]). The coefficients B_{λ,l_t} were obtained for a range of values of k^2, and the results interpolated to desired LF frame energies defined by (3) and the geometric mean $k^2 = k_{vj} k_{v'j'}$. This permitted the use of a *single* set (the calculation of which was one of the most time-consuming parts of the work) of B_{λ,l_t}, obtained over a sufficiently wide energy range, for arbitrary j and j' and incident electron energies.

The evaluation of these coefficients requires the l_t-reduced[11] T matrices:

$$T_{vl,v'l'}^{l_t} = \sum_m (-1)^m C(ll'l_t; m-m)\langle v|T_{ll'}^m(R)|v'\rangle , \quad (4)$$

where m corresponds to the collision symmetry. The elements of $T_{ll'}^m(R)$ from the close-coupling calculations for $l_m > 16$ were augmented by unitarized Born[13] T matrices for $l_m < l \le l_b$, and for $l_t = 1$ and 2 by FBA T matrices[11] for $l_b < l \le l_{max}$. The values of $D(R)$, $Q(R)$, $\alpha_0(R)$, and $\alpha_2(R)$ used to define these Born elements were the same as in the scattering calculations. The values adopted for l_b and l_{max} are discussed below. For the evaluation of the integrals in (4) the vibrational wave functions were calculated using a more accurate potential energy curve,[14] to reduce the errors due to the Hartree-Fock approximation at large R. The calculated and measured[15] values of the vibrationally averaged moments and polarizabilities are given in Table I. The calculated value of $\langle 0|D(R)|1\rangle$ is 65% larger than the measured value, with which the results of more accurate calculations[14] agree; but the two calculated $D(R)$ curves differ significantly only for larger R, the Hartree-Fock results being 10%, 18%, and 35% larger at $R = 2.6$, 2.8, and $3.2a_0$, respectively.

To completely characterize the calculations, it remains only to specify l_b, l_{max}, and λ_{max}, the last term taken in the second sum in (2). For $l_t = 0$ and 2, λ_{max} was taken large enough (30, 20, and 15 for $v' = 0$, 1, and 2, respectively) that the coefficients in (2) (for $l_t = 2$ the difference of the coefficients) behaved as const/λ, and the sum from $\lambda_{max} + 1$ to ∞ was evaluated in closed form. For $l_t = 1$ and 3, $\lambda_{max} = 28$, 25, and 15 was adequate for $v' = 0$, 1, and 2, respectively; for $l_t \ge 4$, we took $\lambda_{max} = 15$. As has been our previous experience, a value of $l_b \ge 2\lambda_{max}$ was required; we took $l_b = 60(55)$, 40(50), and 30(30), for $l_t = $ even (odd) for $v' = 0$, 1, and 2, respectively. For $l_t = 1$ and 2, the contributions to the sum in (2) cancel identically for $l > l_b + \lambda_{max}$ since the FBA is assumed to be valid. This defines l_{max} for

TABLE I. Vibrationally averaged multipole moments used in the present calculations and from measurements (Ref. 15).

	v-$v' = 0$-0	0-1	0-2
$\langle v|D|v'\rangle$	−0.483	−0.0454	0.0032
$\langle v|Q|v'\rangle$	−2.898	−0.242	0.100
$\langle v|\alpha_0|v'\rangle$	17.40	0.622	−0.031
$\langle v|\alpha_2|v'\rangle$	1.38	0.763	−0.011
$\langle v|D|v'\rangle_{expt}$	−0.436	−0.0275	0.0027
$\langle v|Q|v'\rangle_{expt}$	−2.778		

these cases. The calculated values of $\langle v|D(R)|v'\rangle$, $\langle v|Q(R)|v'\rangle$, and $\langle v|\alpha_2(R)|v'\rangle$ were used in the second term in (2) to ensure exact cancellation of contributions for $l > l_{max}$, but the measured values of $\langle v|D(R)|v'\rangle$ were used in the first term in (1) to partially correct for the error introduced by the Hartree-Fock wave function. For $l_t = 0$ and ≥ 3, we took $l_{max} = l_b$.

Results for the total (summed over all final rotational states) integrated cross sections for the transitions v-$v' = 0$-1 and 0-2 are given in Fig. 1. These were obtained from BF frame scattering energies ≥ 0.1 eV, which corresponds in the MEAN approximation to incident energies in the LF frame $\gtrsim 0.38$ and 0.73 eV, respectively, for $v' = 1$ and 2 (thresholds are at 0.36 and 0.70 eV). The measured[1] cross sections (originally put on an absolute scale with reference to the v-$v' = 0$-0 transition) were renormalized by a multiplicative factor of 0.70, as suggested by the earlier[4] comparison of calculated and measured results for v-$v' = 0$-0. The SE results are poor both in shape and magnitude. The inclusion of polarization has a dramatic effect, much larger than for v-$v' = 0$-0,[4] but the SECOP results are still too low. Total differential cross sections for both transitions were found to be very nearly isotropic in the angular range 30 to 120 deg over the entire energy range, consistent with the measured results.

Good results near threshold cannot be expected, owing to the incomplete treatment of nuclear dynamics inherent in the MEAN approximation, but the sharp rise in the cross section near threshold is nevertheless qualitatively reproduced. This justifies some optimism that the threshold feature would emerge in calculations based on a more accurate approximation. We attribute most of the discrepancy away from threshold to the approximate treatment of exchange. Limitations of the FEG exchange model are by now well known, most recently noted[9] in tests of the COP potential for H_2 and N_2. While its failures have never been seen to be so large as in this case, the observed effect of polarization suggests that the limitations of the FEG exchange approximation might also be amplified in vibrational excitation.

As a preliminary test of this hypothesis we compared SECOP results for vibrationally elastic scattering at R_e (equilibrium R, $2.41a_0$) with the earlier results,[4] which used the same model of exchange and an empirically tuned polarization potential (SETP), and with new calculations combining the COP potential with an exact treatment[16] of exchange (ESECOP). The SECOP results for the total integrated cross section were roughly 20% lower than the SETP results,
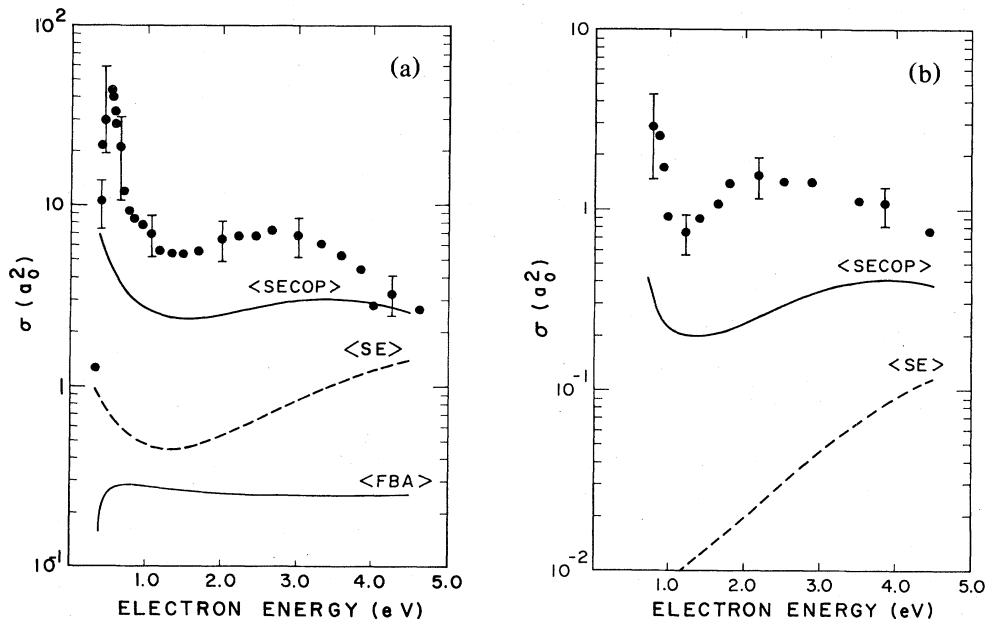
FIG. 1. Total integrated cross sections for the transition: (a) v-v' = 0-1 and (b) 0-2.

with much larger differences for individual rotational transitions. The ESECOP results, on the other hand, were in quite good agreement with the SETP results, even for individual rotational cross sections. Where differences existed, e.g., in differential cross sections, the ESECOP results were marginally better compared to the shape of the measured results. It is clear that, just as for H_2 and N_2, the empirically tuned polarization potential compensated, by being slightly too attractive at intermediate distances, for the weakness of the FEG exchange potential. This is nicely illustrated by

comparing eigenphase sums (Fig. 2). The relative changes in the total vibrationally elastic cross section on going from the SE to SECOP to ESECOP model suggest that a further larger increase in vibrationally inelastic cross sections might be expected when exchange is included exactly. Work to test this hypothesis is in progress.

In spite of the limitations of the present results, we can also draw some tentative conclusions with regard to the other issues mentioned at the outset. The relative insensitivity of the results for v-v' = 0-0 to the model of the interaction
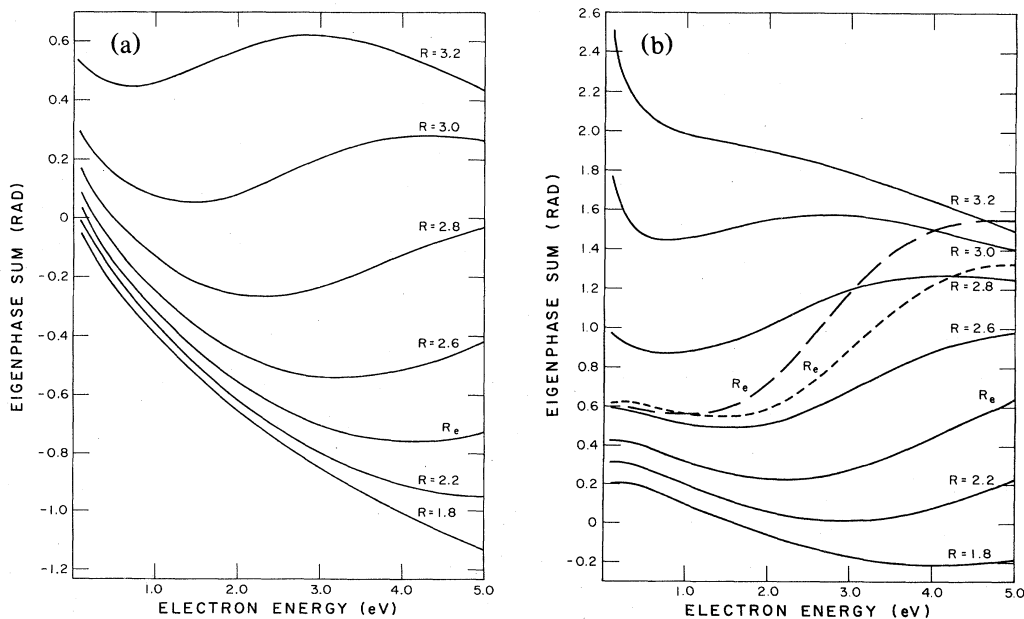

FIG. 2. Eigenphase sums for Σ symmetry scattering for several values of R from (a) SE; and (b) SECOP and ESECOP (short dashes) calculations, and from earlier (Ref. 4) SETP calculations (long dashes).

potential, and the good agreement of the ESECOP and SETP results, adds weight to the suggestion[4] that the reported[1] excitation cross sections should be renormalized by a factor of 0.70, consistent with the reported experimental uncertainty. This is supported by a recent analysis of swarm measurements, in which a normalization factor of 0.75 was used.[17] The isotropy of the measured cross sections has been interpreted as indicative of s-wave scattering. We find, on the other hand, that the dominant vj-$v'j' = 00$-10 cross section near threshold is strongly influenced by p-p and d-d contributions, and that both p-p and s-d scattering contribute significantly to the equally important vj-$v'j' = 00$-$v'2$ cross section at higher energies.

The most controversial issue is the cause of the sharp peak near threshold; Fig. 2 is also interesting in this regard. The threshold value of the eigenphase sum for Σ symmetry scattering by a polar molecule must be finite with divergent slope[18] at zero energy for $D \leq D_c = 0.639$ a.u., and diverges for larger values of D. D_c occurs at $R_c \simeq 2.9a_0$ for the wave functions used in generating Fig. 2, but D for HCl is always less than D_c in fact.[14] Specifically, for $R = 1.8$, 2.2, R_e, 2.6, 2.8, and R_c the threshold values consistent with the present calculations are[19] 0.08, 0.15, 0.21, 0.29, 0.44, and 0.79 rad, respectively. The SE results [Fig. 2(a)] seem to tend to these limits, albeit less rapidly as R increases. With the inclusion of polarization [Fig. 2(b)], on the other hand, the eigenphase sums for $R < R_c$ rise, rather than fall, rapidly from threshold. At R_e, for example, the ESECOP (SECOP) results are 0.304 (0.265), 0.395 (0.302), 0.530 (0.370) rad for energies of 10^{-5}, 10^{-4}, and 10^{-3} Ry, respectively. The change is equally dramatic for $R > 2.9a_0$, radically changing the form of the low-energy eigenphase sums. Were HCl nonpolar we would be justified in suspecting that the ESECOP results indicate a low-energy resonance or virtual state, induced by interactions of intermediate range (p- and d- as well as s-wave scattering), changing to a bound state for $R \gtrsim 2.9a_0$.

We can question, then, whether the polar nature of the molecule is of much relevance (see Herzenberg[3]) to the

behavior of the cross sections at low energies, except perhaps for energies so low as to be of no practical interest. Is, for example, the behavior of the SECOP results for $R > 2.9a_0$ due to the fact that $D(R)$ is (incorrectly) greater than D_c, or to the existence[20] of a rather conventional (chemically bound) HCl$^-$ state for $R \geq 3.0a_0$? To study this question we recalculated the SECOP eigenphase sum for $R = 3.2a_0$ and energies ≥ 0.1 eV, with the dipole term in the expansion of the static interaction potential scaled consistent with the correct[14] ($< D_c$) value of D. The results were within 1% of the curve in Fig. 2(b). This gives us some confidence that the use of a Hartree-Fock wave function introduced little error in the results presented in Figs. 1 and 2 due to incorrect supercritical values of $D(R)$ at large R (as might also be deduced by considering the relatively small contributions from the transition vj-$v'j' = 00$-$v'1$ to the total cross section), and that the bound HCl$^-$ state is primarily responsible for the behavior of the eigenphase sums for $R \geq 2.9a_0$ and energies above 0.1 eV.

Note added in proof. Our suggested[4] renormalization of the measured[1] vibrational excitation cross sections leads to a peak value of 1.23×10^{-15} cm^2 for the $v = 0$-1 cross section. This is not only consistent with the result (1.3×10^{-15} cm^2) from analysis[17] of recent swarm measurements, as noted, but also with the upper limit (1.25×10^{-15} cm^2) of results from trapped electron measurements,[21] and with the value (1×10^{-15} cm^2) deduced from rate constant measurements.[22]

*Permanent address: Quantum Physics Division, National Bureau of Standards, Boulder, CO 80303.

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