Positron-HF Collisions: Prediction of a Weakly Bound State

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Ab initio molecular R-matrix calculations are presented for collisions of low-energy positrons with the hydrogen fluoride molecule as a function of HF internuclear separation. Calculations presented are for Σ total symmetry with and without polarization effects. These calculations mirror recent electron-HF scattering calculations by Morgan and Burke. Strong evidence is obtained for the presence of a bound state of the e^+HF system. The experimental consequences of this result are discussed.

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A striking difference between the behavior of low-energy electrons and positrons in collision with atoms and molecules is the absence in positron scattering of the sharp structures often observed with electrons. These structures are associated with compound states, either bound or resonant, of the total system and often dominate elastic and inelastic cross sections in the low-energy region. Although the possibility of compound states in positron-molecule systems has long been discussed,[1,2] to our knowledge there is as yet no confirmed observation of such a state.

It is well known from both theory and experiment that the cross sections for very-low-energy electrons in collision with strongly dipolar systems such as HF and HCl display sharp peaks near threshold. Recent work on HF by Morgan and Burke (MB)[3] suggests that these structures are due to the presence of a very weakly bound state of HF$^-$. MB found a bound state for all the geometries of HF they studied, including small internuclear separations for which the dipole moment of HF is subcritical, i.e., less than 0.639 a.u. For this case Crawford[4] has shown that no bound states are supported by a potential of simple dipolar form, a conclusion which is unaltered by the inclusion of rotation.[5,6] Actual molecular potentials, however, contain short-range terms due to static repulsion (damping of the dipole) and polarization effects.

As the asymptotic potential of these polar systems is equally attractive to both electrons and positrons, they would seem good candidate systems which might support positron-molecule bound states. Such bound states would have immediate consequences for positron scattering off the system, as the associated nuclear excited Feshbach resonances[7]—caused by vibrationally (or rotationally) excited states of the positron-molecule complex—should lead to very rapid positron annihilation. Indeed a number of small molecules have been observed to be very efficient positron annihilators, having an effective number of electrons available for annihilation ($\bar{Z}_{\text{eff}}$) as high as 15000![8] What causes these anomalously high values of $\bar{Z}_{\text{eff}}$ remains unclear. One possible explanation is the existence of weakly bound states which would give rise to many resonances involving vibration and rotation of the nuclei. We note, however, that only some of the molecules concerned have large dipole moments.

We have performed calculations, at the Born-Oppenheimer level, on the low-energy collisions of positrons with HF using the adaptation of the molecular R-matrix method used previously for e^+-H$_2$ and e^+-N$_2$ scattering.[9] This method represents the molecular target inside the R-matrix sphere, here of radius $10a_0$, with use of a multicenter basis. For HF we used the Slater-type orbitals (STO's) of McLean and Yoshimine[10]; these functions were augmented by a set of numerical continuum functions, represented as a partial-wave expansion about the molecular center of mass, to carry the positronic motion. These functions were Schmidt orthogonalized to the occupied HF target orbitals. Only functions with $l \leq 5$ were retained in the basis. Further details of this method can be found elsewhere.[9,11]

In the static approximation the target electrons are frozen in the ground-state configuration obtained from a self-consistent-field (SCF) calculation and the positron is allowed to occupy all orbitals of the appropriate symmetry. Short-range polarization effects are included by allowing one-particle excitations of the target with the positron occupying appropriate target orbitals. For calculations of Σ total symmetry, Σ polarization effects are given by target excitations which retain the Σ symmetry of the target and Π polarization involves $\sigma \leftrightarrow \pi$ excitations of the target.

Outside the R-matrix sphere the potential due to the target is represented as a multipole expansion. For HF the leading term is the dipole, but long-range polarization can also be accounted for by including the target polarizabilities, $\alpha_0 = 5.6a_0^3$ and $\alpha_2 = 0.993a_0^3$.[12] The target quadrupole was also included in the asymptotic potential.

Figure 1 shows eigenphase sums for low-energy e^+-HF collisions with Σ symmetry at the HF equilibrium bond length of $1.733a_0$ as a function of model. As one would expect the calculated eigenphase sum increases as polarization effects are introduced into the calculation. For all the models the eigenphase sums are sharply

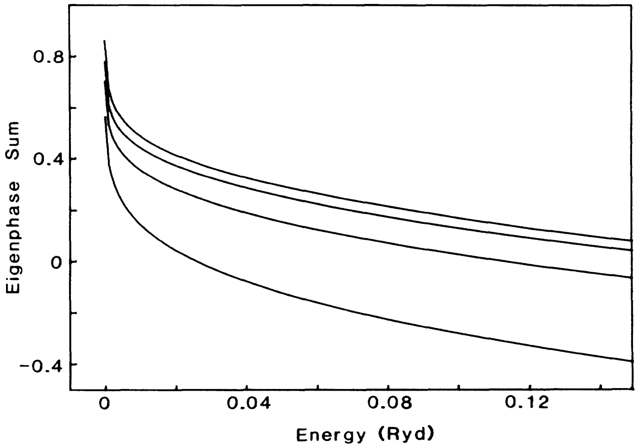

FIG. 1. Positron-HF eigenphase sums for various models at the HF equilibrium separation. The lowest eigenphase sums are for the static approximation, then for static plus short-range Σ polarization only, short-range Σ+Π polarization, and the largest eigenphases are for the inclusion of both short- and long-range Σ+Π polarization.

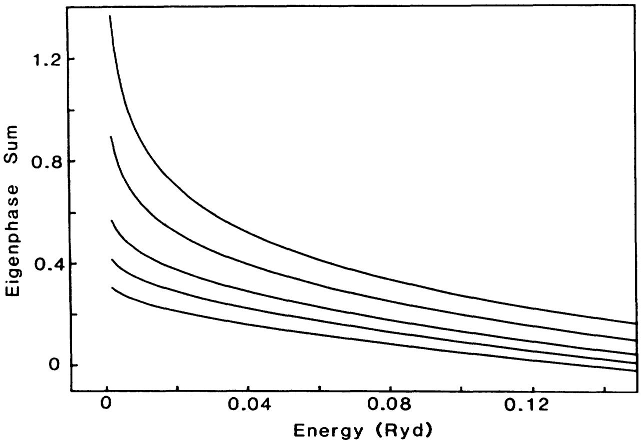

FIG. 2. Positron-HF eigenphase sums for five HF bondlengths, R. The values of R used are $(1.3, 1.5, 1.733, 2.1, \text{and } 2.5)a_0$; the eigenphase sums increase with increasing R. The calculations are for the static plus short-range Σ+Π polarization approximation.

peaked near threshold. This behavior is known to be associated with the presence of a bound state.[3,13] In particular, by Levinson's theorem,[14] one would expect the eigenphase sum to approach zero in the absence of a bound state.

Figure 2 shows the behavior of the eigenphase sums as a function of HF internuclear separation, R. The HF dipole increases with R and is subcritical for bond lengths less than $1.4a_0$. Even so we still find that the eigenphase sum is sharply peaked at threshold for all geometries including $R=1.3a_0$. This behavior is contrary to that observed in electron-HCl calculations where the eigenphases are peaked at threshold for long bond lengths and dip sharply at threshold for shorter bond lengths.[13] This latter behavior is associated with the presence of a virtual state.

In order to confirm the existence of a positron-HF bound state and to obtain an estimate of the binding energy, we have searched the complex k plane for S-matrix poles, using complex boundary conditions.[3] The results are presented in Table I; for comparison the corresponding results for the electron-HF calculations of MB are also given.[3] We did not attempt a comprehensive search of the complex plane, but limited ourselves to inspecting the behavior near threshold. In this way we were able to obtain poles on the positive imaginary axis for each geometry, provided k was greater than 10^{-5} a.u. Our calculations gave no evidence for other bound states or low-lying resonances, though the former may be expected with very small binding energies.[4]

For comparison we give the target SCF energy obtained for each geometry and the relative energy of the lowest R-matrix pole for both these and MB's calculations. An R-matrix pole below the target energy can be taken to imply the presence of a bound state due to the short-range potential inside the R-matrix sphere. Such a case is observed for the e^--HF system at large R, but not for e^+-HF. This implies that the binding in the e^+-HF case is largely due to the long-range potential.

It is notable that a positron binds more strongly to HF

TABLE I. Binding energies and lowest R-matrix pole positions, in Ryd, as a function of HF internuclear separation R for the positron-HF and electron-HF systems relative to the SCF energy of the HF target.

		Electron-HF[a]		Positron-HF	
R (a_0)	Target energy (Ryd)	Pole position	Binding energy	Pole position	Binding energy
1.3	−199.94266	0.0235	$< 10^{-10}$	0.0176	$< 10^{-10}$
1.5	−200.10580	0.0203	$< 10^{-10}$	0.0154	$< 10^{-10}$
1.733	−200.14092	0.0154	1.2×10^{-8}	0.0131	3.4×10^{-8}
2.1	−200.06758	−0.0024	0.00098	0.0092	0.000025
2.5	−199.94238	−0.0579	0.05089	0.0046	0.000358

[a] Ref. 3.

at its equilibrium separation than an electron. This would appear to be due to the direction of the dipole potential which enhances the interaction of the positron with the more polarizable F atom.

Our calculations thus strongly indicate the presence of a bound state in the positron-HF system. As our calculations are *ab initio*, no assumptions have been made in including target polarization or other effects. It must be recognized that the inclusion of polarization in positron-molecule calculations is still an unsolved problem[15] and much work remains to be done in this area. However, the polarization interaction is purely attractive and any underestimate of it due to only partially including polarization effects will serve only to underestimate the positron-HF binding energy. We are therefore confident that the effect we are predicting is real and not just an artifact of an imperfect calculation.

The experimental consequences of a e^+-HF bound state are likely to be significant. The elastic e^+-HF cross section is large at low energies (we calculate $1252a_0^2$ at 0.01 Ryd) and is unlikely to be significantly altered by the presence of nuclear Feshbach resonances. However, a positron trapped in such a resonance will annihilate with great efficiency leading to anomalously large values of $\bar{Z}_{\text{eff}}$. Accurate theoretical estimates of resonance parameters and then $\bar{Z}_{\text{eff}}$ require calculations which allow for vibration and rotation of the target. Because of the low energies involved, these nuclear motion effects ought to be included nonadiabatically. At this level of approximation MB found no qualitative change in the binding energy of HF^- with vibrational motion.

The problem of extending the *R*-matrix method to include rotational motion nonadiabatically has yet to be fully addressed, although we should expect that the collision will be *sudden* except for very low energies comparable to the rotational spacing.[16] Conversely, for a bound state one would expect the complex to rotate as a whole, thus leaving the dipole potential largely unmodified. A comprehensive study including effects due to nuclear motion and higher total symmetries will be the subject of further work.

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